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FAT RANCIDITY

Summaries of Papers presented at the 2nd Scandinavian Symposium on Fat Rancidity

Edited by Aage Jart

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Summaries of papers presented at the

2nd Scandinavian Symposium on Fat Rancidity

Editor

Aage Jart

Danish Fat Research Institute

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Chemistry including Metallurgy series

New Series Ch. 1

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PREFACE

The present papers are summaries of lectures (in some cases supplemented with information from the following discussions) given at the 2nd Scandinavian Symposium on Fat Rancidity held in Elsinore, Denmark, 9 - 11 September 1957. 86 fat scientists and technologists from the Scandinavian countries participated. The subject of the symposium was: The microbial and oxidative rancidity of fats as well as other changes reducing the quality during production, storage and transport.

The lectures in extenso (with 140 illustrations and tables as well as references and summaries of the discussions) have been published in the Scandinavian languages by the Danish Academy of Technical Sciences (Price: 40 Danish kroner).

I wish to thank Mr. Hans Sørensen, M.Sc., for his valuable assistance during the preparation of this publication.

Copenhagen, January 12, 1959.

AAGE JART

Editor

FAT RANCIDITY

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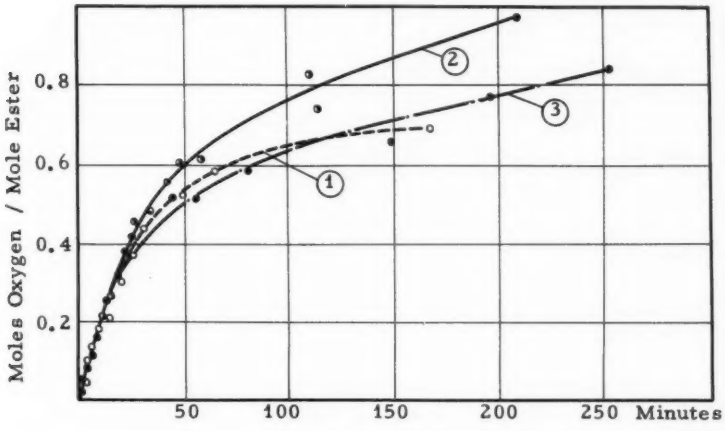
LIPOXIDASES.

S. BERGSTRÖM
Professor, Lunds Universitet, Sweden.

In the usual autoxidation of unsaturated fatty acids the oxidation rate is highly increased with increasing number of double bonds, and the oleic acid reacts comparatively slowly.

It is characteristic of the enzymatic reaction by lipoxidase that oxygen will attack linoleic, linolenic and arachidonic acid at nearly the same rate (Holman, fig. 1), and only in a single point of the molecule. Oleic acid and saturated acids will not react at all. The three first mentioned acids have a structure consisting of double bonds with a methylene group in between. The two double bonds in the linoleic acid have cis-configuration. A linoleic acid with one or two trans double bonds will not react. An interesting fact is that the cis-trans linoleic acid will have a restrictive influence on the enzymatic oxidation of the cis-cis acid. Another characteristic of the enzymatic reaction is the nature of the hydroperoxides formed. Unlike those from the usual autoxidation, the substances from the lipoxidase reaction possess optical activity.



① Ethyl linoleate

② Ethyl linolenate

③ Methyl arachidonate.

Figure 1.
Lipoxidase oxidation of fatty esters at 13°C.

NDGA (nor-dihyuroguaiaretic acid) and propyl gallate have excellent antioxidative properties as regards the effect of lipoxidase. When the reaction, with NDGA present, is followed by measurement of the light absorbance at 232 mμ (formation of conjugated double bonds), it appears that the fatty acids are practically not attacked. However, the system will also in this case absorb oxygen and the NDGA will be oxidized. Perhaps the linoleic acid in this case is a coenzyme for the oxidation of the NDGA.

The lipoxidases are mainly found in fat-containing seeds. It has been mentioned in literature that the enzyme was found in animal tissues, but to-day we have no definite evidence of this.

THE EFFECT OF LIGHT ON EDIBLE OILS.

K. HELHOLT.
Head of laboratory, A/S Aarhus Oliefabrik, Denmark.

Some edible oils get a peculiar, rubberlike taste when they are exposed to light.

In some cases this "rubber taste" develops extremely fast, in other cases slowly, and in still other cases it does not develop at all.

Without irradiation the rubber taste does not arise.

Table 1 gives a rough guide regarding the sensitivity to light of some oils when they are exposed to sunlight.

Oil	Rubber taste develops after:	Rubber taste is not developed after:
Groundnut-	30 seconds to 30 minutes	
Rapeseed-	20 to 30 seconds	
Sesame-	30 seconds to 30 minutes	
Soybean-	75 seconds	
Coconut-	- 10 minutes	
Palm-	- -	60 minutes
Hydrogenated Coconut-	- -	60 "
Hydrogenated Whale-	- -	60 "

Table 1.

IRRADIATION of EDIBLE OILS with SUNLIGHT.

The difference in the light sensitivity of the nonhydrogenated oils may depend on

1. The effect of variation of soil, manure, etc., on the parent plant.
2. Changes of the oil in the raw material through deterioration of the seeds.
3. Impurities in the raw material.
4. Impurities in auxiliary materials used
   a. during extraction or
   b. during refining of the oils.

In some cases sulphur and sulphur-containing compounds seem to intensify the development of the "rubber taste".

Experiments made with irradiation of rapeseed oil with ultraviolet light at 30°C. showed that irradiation developed a faint rubber taste in the course of one minute; and after 2 minutes this taste was extremely disagreeable.

The rubber taste became stronger and stronger the longer the oil was irradiated.

Only after 30 minutes did the oil give a weak peroxide reaction. (Table 2).

When the irradiated oil had been stored in darkness in closed glasses the rubber taste disappeared. (Table 3).

A new irradiation developed the rubber taste again.

	No irradiation	Time of Irradiation								
		Minutes					Hours			
		1	2	5	10	30	1	2	3	6
Peroxide value	0	-	-	0	-	0	0	0.8	0.9	1.0
Kreis test	0	-	-	0	-	0	0	0	0	0
Acid value	0.05	-	-	-	-	-	-	-	-	0.05
Iodine value	104.5	-	-	-	-	-	-	-	-	104.9
Rubber taste	0	1	2	3	3	3	4	4	4	4
		→ Increasing rubber taste								

Table 2.

Edible Rapeseed Oil in Quartz Tubes Irradiated with Ultraviolet Light at 30°C.

	Time of Irradiation								
	Minutes					Hours			
	1	2	5	10	30	1	2	3	6
After storing for:									
6 hours	g = 0	g = 0	g = 0	g = 0	g = 3				
24 "	-	-	-	-	-	-	g = 3	g = 3	g = 3 P=1.2
96 "	-	-	-	-	-	-	g=0 P=0.8	g=1 P=0.9	-
120 "	-	-	-	-	-	-	-	-	g=0 P=1.2
	None of the samples gave a Kreis reaction.								

Table 3.

The Same Oils as in Table 2 after Irradiation and Storage in Darkness.
g = rubber taste. P = Peroxide value.

By desodorization the rubber taste also disappears, but in this case, too, it arises by repeated irradiation.

Hydrogenation of the rapeseed oil makes it immune to this effect of the light. (Table 4).

Hydrogenated Units[1]		Before Irradiation	Irradiated. Hours		
			$\frac{1}{2}$	1	6
3	Peroxide value	0	-	-	1.2
	Kreis test	0	-	-	0
	Iodine value	101.2	-	-	101.2
	Rubber taste	0	0	0	0
	Taste (2)	8	8	7	3 oxidized
5	Peroxide value	0	-	-	1.0
	Kreis test	0	-	-	0
	Iodine value	99.6	-	-	98.7
	Rubber taste	0	0	0	0
	Taste	8	8	8	3 oxidized
38	Peroxide value	0	0	-	0
	Kreis test	0	0	-	0
	Iodine value	66.6	-	-	-
	Rubber taste	0	0	-	0
	Taste	7	7	-	5 hydrogenated

Table 4.

Hydrogenated Edible Rapeseed Oil in Quartz Tubes Irradiated with Ultraviolet Light at 40°-44°C. ([1] Units of reduction of the original iodine value 104.4. [2] The numbers correspond to the 10-scale in which 10 is the highest value).

Neither hydrogenated coconut oil nor hydrogenated whale oil develops a rubber taste on irradiation.

Rapeseed oil saturated with oxygen before irradiation gave the same rubber taste as oil without oxygen. (Table 5).

	Before Irradiation	Irradiated in Vacuum	Irradiated in Oxygen
Peroxide value	0	0	0
Kreis test	0	0	0
Acid value	0.14	0.14	0.14
Iodine value	104.7	104.7	104.7
Taste	normal	rubber	rubber
After storing in darkness for 4 hours	Taste is unchanged	Rubber taste has disappeared	
	No change in the chemical analysis		

Table 5.

Edible Rapeseed Oil Irradiated with Ultraviolet Light for 15 min. at 30°C in Vacuum and Oxygen, respectively.

Some examples of the importance of knowing this peculiar effect of light on edible oils are mentioned.

From the discussion it appeared that no difference in the occurrence of a rubber taste could be found in the case of soybean and rapeseed oil - dependent upon whether or not lipoides were present.

OXIDATIVE CHANGES IN DAIRY PRODUCTS.

P. SWARTLING

Professor, Statens Mejeriförsök, Alnarp, Sweden.

Among defects in flavour of dairy products those listed in Table 1 are considered to be caused by oxidation of the unsaturated fatty acids in triglycerides and phospholipides. This opinion is based on several facts: The defects do not develop in products as butter and dried milk if manufactured and stored, respectively, in inert atmosphere or in degassed milk. The frequency and intensity of the defects increase with increasing bacteriological quality and are very often found in freezer stored products.

Product	°/o lipids	Flavour defects
Whole milk	3.0-3.5	metallic, oxidized flavour
Skim milk	0.05	" "
Cream	12-40	" , tallowy
Butter milk	0.30	"
Butter	82-83	" , oily, fishy, tallowy
Cheese	16-29	(metallic)
Dried milk	28	metallic, tallowy
Evaporated milk	9	"

Table 1.

Flavour defects caused by lipid oxidation.

Close correlation (+0.65 - +0.75) has been repeatedly shown to exist between intensitv of flavour defects and peroxide values of the fat fraction. Oxidation products isolated from stored butter show a close connection between peroxide values and light absorption at 232 mμ (Fig. 1).

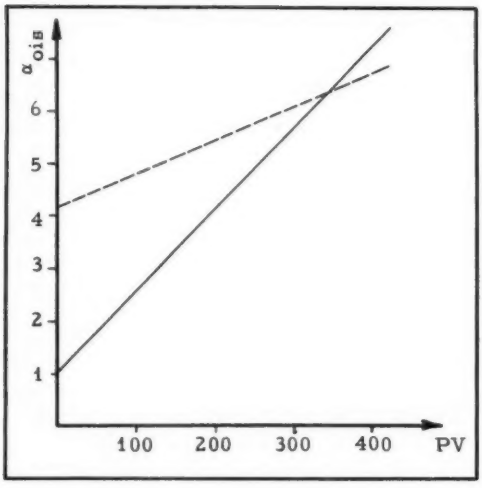


Figure 1.

Peroxide value and absorption at 232 mμ for oxidation products from butter with oily flavour.

Secondary oxidation products found in milk fat, oxidized milk phospholipides, as well as milk and butter have been shown to be mainly α-, β-unsaturated carbonyl compounds (Tab. 2).

Milk fat oxid. at 70°	C_7-C_{12} α-, β-unsaturated ketones	Keeney and Doan, 1951
Milk fat oxid. at 100°	mono-en, di-en, conj. and non-conj. carbonyl compounds	Tamsma, 1955
Milk phospho-lipides	5 diff. saturated and unsaturated carbonyl compounds	Riel and Sommer, 1955
Milk	C_5-C_{11} α-, β-unsaturated aldehydes C_4-C_{11}-2-4-dienal (2-4-hexadienal)	Forss et al., 1955
Butter	unsaturated C_6-C_8-aldehydes methyl ketones	van der Waarden, 1947
Butter	α-, β-unsaturated carbonyl compounds	Holm et al., 1952

Table 2.

Off-flavour compounds found in oxidized milk lipids and dairy products with relevant flavour defects.

Unsaturated fatty acids in milk triglycerides and phospholipides consist of oleic acid (28-31 %) and several poly-unsaturated acids. These are listed in Tables 3 and 5. In Table 4 the proportions of three main groups of milk phosphatides are given.

Acid	Mattsson et al. (1951)	Stadthouders and Mulder (1955)
Conj. C_{18}	0.6-2.4	0.6-2.8
Linoleic	0.7-1.7	0.7-1.9
Linolenic	0.6-1.5	0.4-1.0
Arachidonic	-	0.3-0.6

Table 3.

Content of poly-unsaturated fatty acids in milk triglycerides.

	Phosphatidyl-cholin	Phosphatidyl-serin + ethanolamine	Sphingo-myelin
Kurtz et al., 1934	60	32	8
Lobstein et al., 1940	50	25	25
Baliga et al., 1955	30	45	25

Table 4.

Relative content of various phosphatides in milk.

Acid	Phospholipides	Triglycerides
Conj. C_{18}	0.6-0.8 ?	0.4-0.7
Linoleic	2.9-4.3	0.8-1.3
Linolenic	0.3-0.7	0.4-0.5
Arachidonic	3.1-3.9	0.4-0.5

Table 5.

Contents of poly-unsaturated fatty acids in phospholipids and triglycerides (winter values, Mattsson, 1957).

The oxidation rate of esters of unsaturated acids is basically determined by the degree of unsaturation (Fig. 2) and by the concentration of the unsaturated ester (Fig. 3). In the dairy products these factors are masked by a variety of other factors, e.g. light, copper, and other possible prooxidants, natural antioxidants and the colloid structure of the products. However, in pure milk fat depleted of antioxidants by coal filtration the oxidation rate increases with increasing content of poly-unsaturated acids (Mattsson et al., 1951).

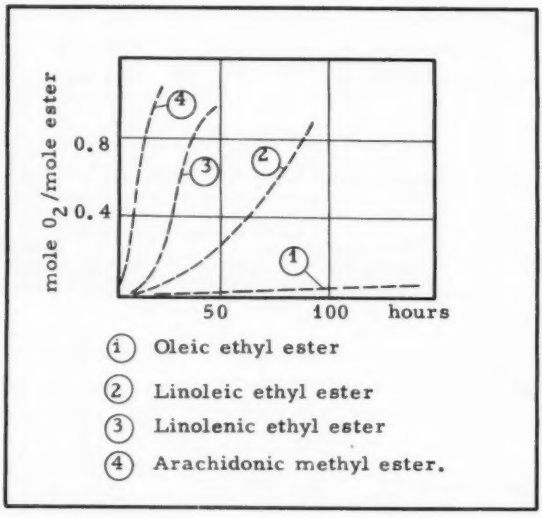


Figure 2.
Rate of oxygen uptake for various unsaturated fatty esters (Holman and Elmer, 1947).

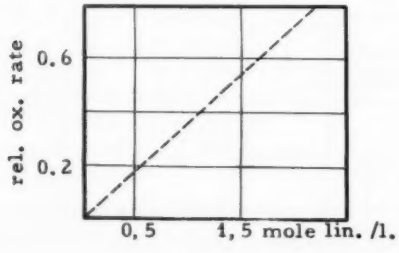


Figure 3.
Rate of oxygen uptake in mixtures of ethyl linoleate and ethyl stearate (Bolland, 1948).

The content of phospholipides in various dairy products is tabulated in Table 6.

	In %	In % of total lipid
Milk	0.030	1
Skim milk	0.015	30
Cream	0.16	0.5
Buttermilk	0.12	40
Butter	0.20	0.3

Table 6.

Content of phospholipides in various dairy products (approx. values).

In most dairy products the position of milk phosphatides in the interfacial layer between triglycerides and the water phase causes a high local concentration of unsaturated material. It is therefore logical to assume that the phosphatides play an important role in the oxidation reactions. This is also the case in whole milk as shown in Table 7.

	Iodine value			
	triglycerides		phosphatides	
	normal	oxid.	normal	oxid.
Swanson and Sommer, 1940	33.1	32.8	48.7	33.7
Koops, 1956	45.0	44.9	60.0	48.2
	41.7	41.3	55.6	45.4
	40.8	40.8	51.8	47.5

Table 7.

Iodine value for fat and phosphatides for fresh and oxidized cream.

In butter, oxidation proceeds at a higher rate at a low pH than at a high pH in the water phase. According to Swartling and Mattsson (Swartling, 1954) Warburg measurements on methyl linoleate (or butter fat) in buffer solutions have shown the oxygen uptake to be faster at a high pH than at a low pH (Fig. 4). Methyl linoleate emulsified with milk phosphatides, however, oxidizes principally in the same manner as butter with regard to the influence of the pH (Fig. 5), which shows the central position of the phosphatides in butter oxidation. These findings have been confirmed later by Koops and Pette (1956).

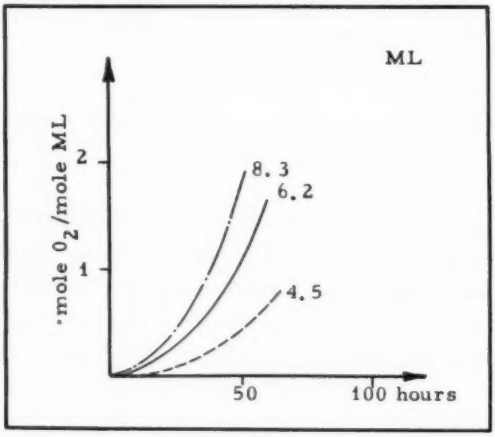


Figure 4.

Rate of oxygen uptake of methyl linoleate emulsified in buffer solutions at various pH (Swartling and Mattsson, 1956).

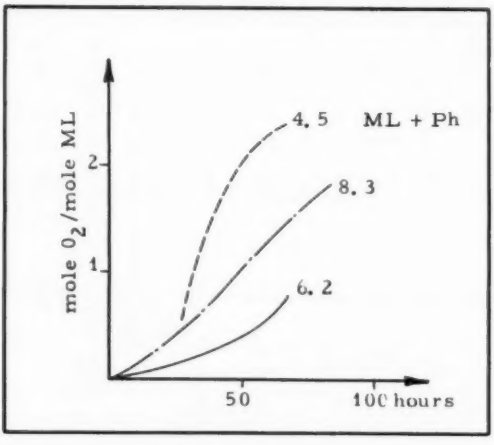


Figure 5.

Rate of oxygen uptake of methyl linoleate and milk phosphatides at various pH (Swartling and Mattsson, 1956).

Some interesting results have been obtained by Lea (1957) in investigations concerning the rate of oxidation of egg phosphatides (Fig. 6).

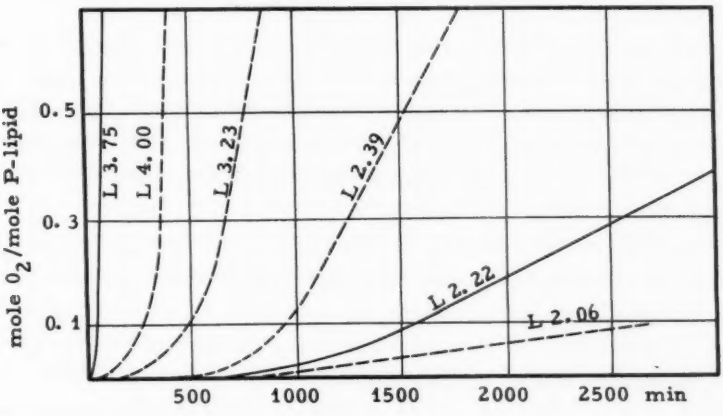


Figure 6.

Relative rates of oxidation of egg phosphatides.
L = lecithin; (2.06 etc. = double bonds per molecule).
(Lea, 1957).

Attention was drawn to the importance of increasing our knowledge of the composition and oxidation properties of the milk phosphatides as well as to the necessity of investigating dairy products in regard to natural antioxidants and prooxidants other than copper, e.g. haemin compounds.

During the discussion it was mentioned that the conjugated C_{18} acid (Tables 3 and 5) is assumed to have 3 double bonds.

OXIDIZED AND SUNSHINE FLAVOUR IN MILK.

K. E. THOMÉ
Professor, Alnarpinstitutet, Alnarp, Sweden.

The difference between spontaneous and Cu-induced oxidized flavour and light-induced sunshine flavour in milk was pointed out. Both types of oxidized flavour result from an oxidation of the di- and polyenic fatty acids in the phospholipids of the fat globules in the milk. The sunshine flavour is the result of this reaction in combination with an oxidative decomposition of the milk protein.

When the di- and polyenic fatty acids are oxidized the resulting flavour compounds are unsaturated aldehydes and ketones, mono- and dienes, often with a short carbon chain of about 5-11 C. They have a characteristic flavour and give an oxidized flavour when added to milk. The concentration of those compounds in milk is about $1:10^7$-10^9. The oxidative protein decomposition concerns certain sulphur-containing amino acids in the protein chain as methionin. The reaction is a decarboxylation and desamination and leads to sulphur-containing aldehydes with a characteristic flavour which gives a typical sunshine flavour when added to milk. The concentration of these compounds is about $1:10^6$.

Different factors influence the rate of both these reactions. The main factors influencing the oxidation of the fatty acids are: total content of unsaturated fatty acids and their degree of unsaturation, the redox-potential of the milk and different factors influencing the redoxpotential as well as prooxidants and antioxidants present in the milk. It is important that the rate of development of off-flavours in milk is more dependent upon the length of the induction period than upon the real rate of the oxidation reaction during the active period.

The oxidative decomposition of the protein which leads to formation of sulphur-containing aldehydes is a photooxidation. Riboflavin is necessary for the transference of the light energy. An interesting question which is not quite clear is how the reacting amino acids are liberated from the protein chain. Even the redoxpotential and factors influencing it are of importance to the rate of this reaction.

When whole milk is exposed to light both these reactions can take place and the formation of oxidized and sunshine flavour in milk is an example that flavour defects even in fat-containing foods can have several reasons and are not always the result of a mere fat oxidation.

THE INFLUENCE OF RANCIDITY IN CEREAL PRODUCTS.

D. KARP

Director, AB Wasa Spisbrödsfabrik, Filipstad, Sweden.

The comparatively small proportion of fat in cereal grains is of great importance from the nutritional standpoint. The abundance of vitamin E (tocopherols as electron carriers) and of essential fatty acids in cereal germs has aroused keen interest in the fields of biology and preventive medicine. But it should also command attention in the technology of modern breadmaking, especially as regards wholemeal products.

It is possible to achieve the manufacture of a wholesome bread with a good taste and reliable keeping properties only if undamaged grain is used as raw material. This is absolutely imperative, so that the original pattern of essential substances in the grain can be obtained and then maintained in its optimal integrity through all the different stages of breadmaking up to the final production of a staple product, which is not only acceptable to the public but also has a long shelf life.

The highest content of linoleic acid, which is the most important essential fatty acid, was detected in rye germ oil, 80 °/o (W. Halden).

The highest content of tocopherols, vitamin E (antioxidants), is found in undamaged grains, 5 - 6 mg °/o.

To obtain these tocopherols and other protecting properties, many improvements can be made. The seed-breeding experts can work by known methods to produce a better resistance against sprouting.

The farmers can harvest at the right time i.e. as early as possible. Drying can be carried out to give better vitality to the grains and stability to the germ fat, by avoiding the now known critical temperatures (wheat, rye and barley) during the drying process (Lindberg). By taking these steps, together with careful grain handling, a several months longer shelf life can be obtained for the baked cereal product.

All these facts have been proved statistically by market investigations using organoleptical two-kinds tests, combined with determinations of the peroxide values of the extracted fat in whole-meal bread (Figure 1).

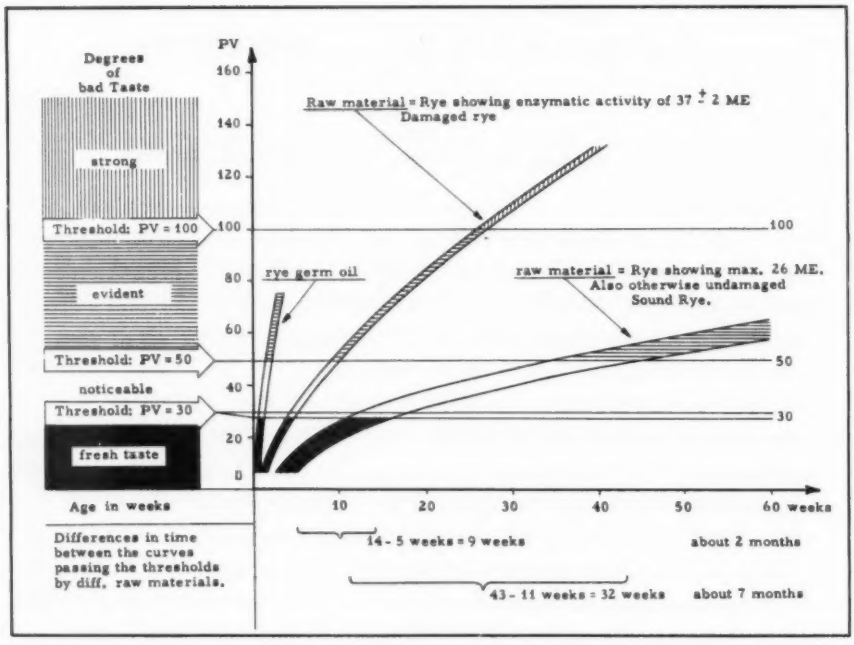


Figure 1.

The peroxide values (PV) for crispbread (market-samples) by damaged resp. undamaged rye.

The freshly baked product has almost always a good taste and flavour and its peroxide value, PV (according to Lea), has always been ~ 0 in hundreds of determinations and independent of how much the raw materials were damaged.

Cold extractions were made here by mechanical shaking in cylinders of stainless steel with bullets and chloroform. (Albertsson).

Peroxide values of 30, 50 and 100 PV are the respective threshold values for passing from fresh taste to "noticeably", "evidently" and "strongly" bad taste.

The peroxide threshold values for bad taste in crispbread, converted into the amounts of oxidized substances that are created by its fat and counted in the whole bread substance, have about the same dimensions as for the taste deterioration in an ordinary fat. (Figure 2).

PV (threshold)		Oxidized fatty acid(ppm)	
ml 0.002 n $Na_2S_2O_3$ per gram fat	(Milliequivalents per kg fat) "Lea"	per fat substance	per bread substance
30	(60)	8 400	168
50	(100)	14 000	280
100	(200)	28 000	560

Figure 2.

Remark: By toasting breads whose PVs have had values in the vicinity of the highest two thresholds, they acquire a new fresh taste again and the peroxide values are 0 after toasting.

Under normal conditions in the market the first two taste-thresholds are crossed several months earlier by a bread manufactured from a damaged raw material. Therefore, such damaged raw material should not be used in the manufacture of staple goods like rye crispbread and similar wholemeal products. (See Figure 1).

RAPID DETERMINATION OF FAT STABILITY WITH REGARD TO OXIDATIVE RANCIDITY.

R. MARCUSE

Head of laboratory, Svenska Institutet för Konserveringsforskning, Göteborg, Sweden.

The testing of fat stability with regard to oxidative rancidity was reviewed. Such testing may have two different purposes, one being to predict shelf-life of fats (or fatty foods), the other to examine the effect of different factors, especially the efficiency of antioxidants. The testing procedure has to include acceleration of the normal process of rancidification and detection of the degree of rancidity at certain time intervals. A requirement for a satisfactory method - especially when testing for prediction of shelf-life - is that acceleration should not change the character of the process of rancidification, i.e. the relative stability of different samples under normal storage conditions must remain unchanged also under accelerating circumstances. Several means have been proposed for acceleration: rise in temperature as well as a stronger illumination or a higher supply of oxygen. However, they all can influence the character of rancidification and, consequently, change the relationship between the stabilities of different samples. For examination of the efficiency of antioxidants, standardized methods may be suitable even if the conditions differ from the normal ones, but for prediction of shelf-life, the testing circumstances should be as realistic as possible. For instance, fats from fat containing food should be tested in their natural milieu, i.e. in the food itself.

For determination of the degree of rancidity, the peroxide value method is the one most commonly used. It is, however, not completely satisfactory, especially since the peroxides are only intermediate products, not responsible for rancid flavour. Other methods used are especially: determination of carbonyl compounds and of oxygen consumption.

The best standardized method for rapid determination of fat stability is the Swift test or "Active Oxygen method". Various modifications regarding details of the apparatus and the way of measuring the degree of rancidity as well as the reliability of the procedure were discussed. In the author's experiments, 1 hour of Swift test corresponded to about 20 days of storage under more normal conditions. The test is to be regarded as a valuable, although not exactly quantitative method.

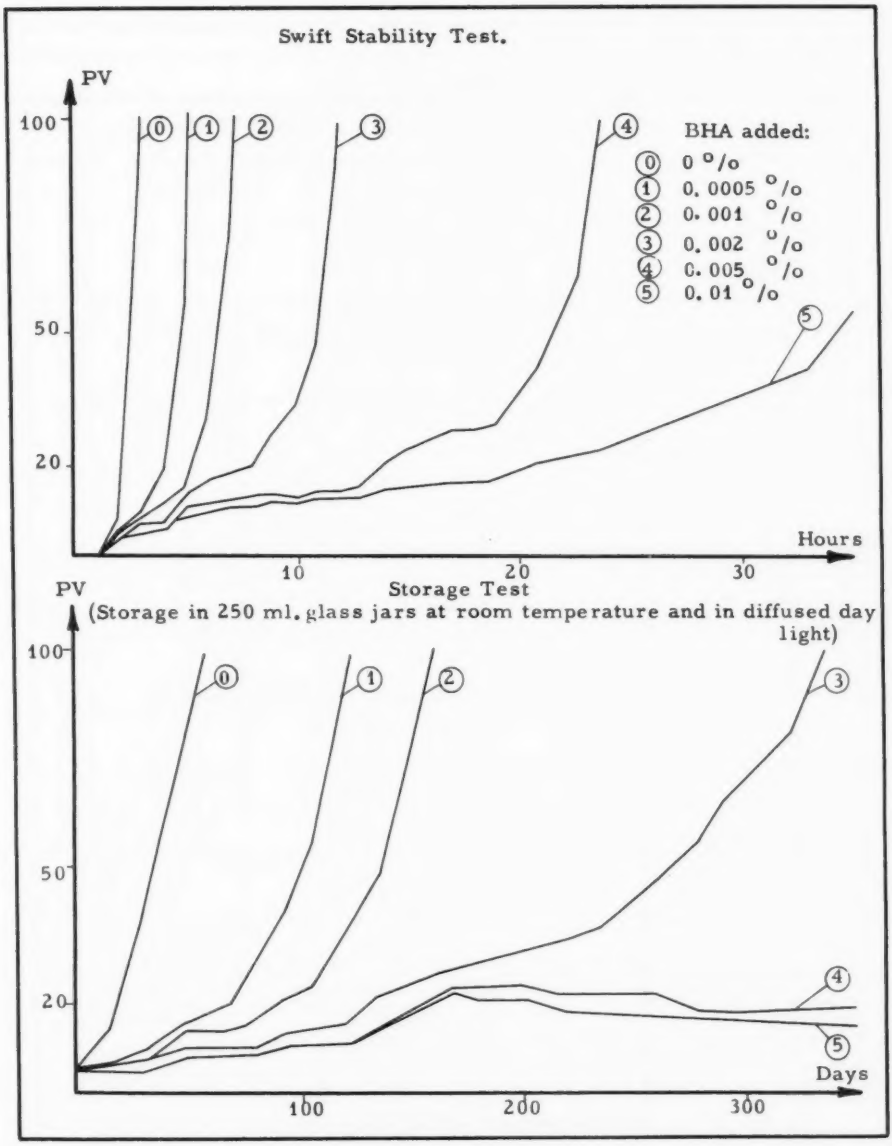


Figure 1.

Examination of stability.

Lard with and without addition of BHA.

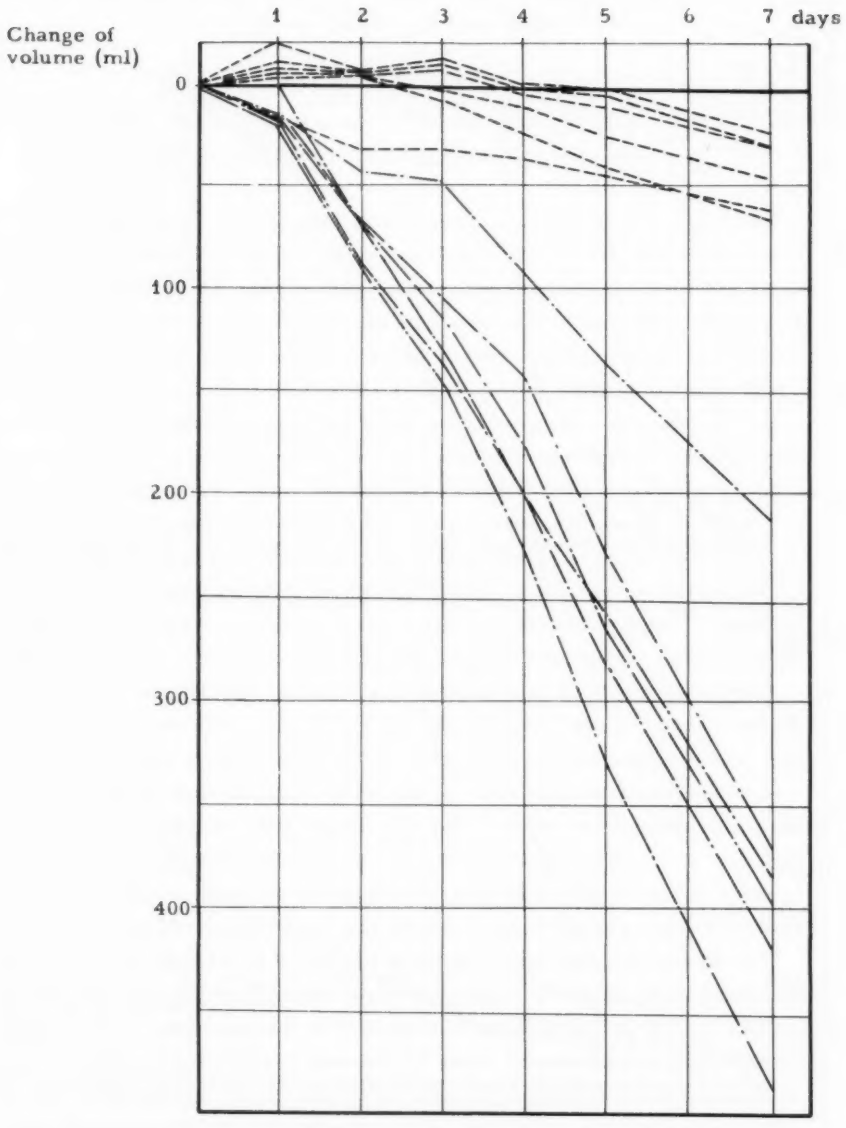


Figure 2.

Determination of stability of salted herring. Volumetric measurement of oxygen consumption. 1 kilo samples of filleted herring in 2 liter jars at 15°C.
6 duplicates with and without the addition of antioxidant.

Several procedures have been elaborated for continuos measurements of the consumption of oxygen. Some of them were described. A simple volumetric method has been used for testing the oxidative stability of salted herring under accelerating conditions. The results of experiments with and without added antioxidants were shown (Fig. 2 and 3). Differences between differently treated herrings were verified by storage tests.

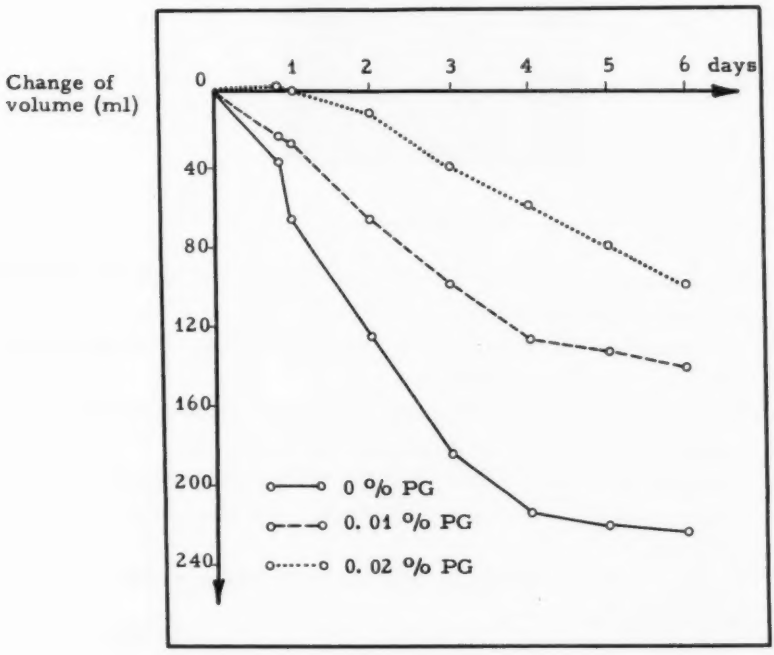


Figure 3.

Determination of stability of salted herring. Volumetric measurement of oxygen consumption. 1 kilo samples of filleted herring in 2 liter jars at 15°C.

Average values of 3 duplicates without the addition of antioxidant and with the addition of 2 concentrations of propylgallate.

Experiments have been started to examine the possibility of using illumination as an accelerating factor, and the apparatus used for this work was shown. (Fig. 4).

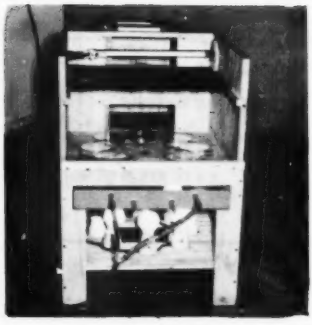


Figure 4.

Apparatus (without cover) for studying the effect of light on rancidity at a constant temperature.
Air circulated by fan in the side tube (on the back of the apparatus) and warmed up by a heating rod.
Temperature regulated by contact thermometer (not shown).
Illumination by lamp-bulbs, underneath.
Temperature and illumination measured and recorded by thermocouples and photocells connected to a Micromax recorder.
Running water as heat filter between bulbs and samples.
Samples in Petri dishes.

Finally, methods of accelerating rancidity by distribution of the fat on an inert carrier, especially filter paper, were discussed. Preliminary results of measuring the colour intensity of the spots obtained with Täufel's method were reported (Fig. 5). This method has further been adapted for testing the synergistic effect of water-soluble substances on the action of oil-soluble antioxidants.

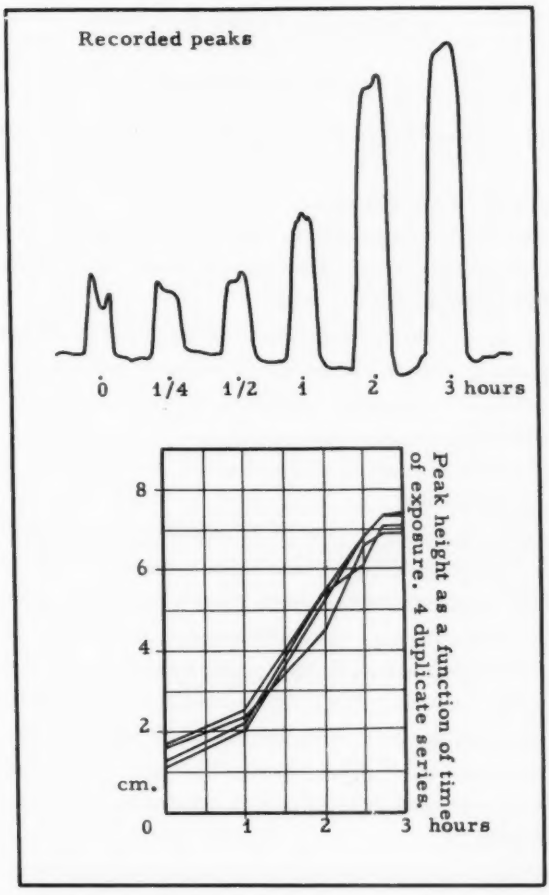


Figure 5.

Measurement and recording of colour intensity of fat spots (1.25 mg herring oil on 4.4 cm^2) by Chromatometer Lange. Spots sprayed with solution of NH_4CNS and $FeSO_4$ (according to Täufel and Vogel) after different times of exposure to diffused daylight.

STABILITY TESTS IN LARD.

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In pure lard biological decompositions are unimportant, while autoxidation is very destructive. This process is due to the high content of unsaturated acids (oleic- and linoleic acid) and the scarcity of natural antioxidants (tocopherols) in lard.

A Swift apparatus is described. A procedure is used in which the gas which escapes from the aeration tubes is bubbled through an aqueous solution of a pH-indicator. The end of the induction period can be estimated by the change in the indicator colour. In the case of lard this change occurs at peroxide values of about 20 - 28 meq. of peroxidic oxygen per kilo of fat.

The average stability at 97.8°C (AOM-stability) for Danish lard is 4.5 hours, corresponding to nearly 4 months at 20°C for 12.5 kilos lard blocks. Several antioxidants were tested in lard by the Swift apparatus. The gallates, specially ethylgallate, very strongly retard the formation of peroxides, while the effect of butylhydroxyanisol (BHA) is less. BHA will delay the secondary decomposition of peroxides, as a rancid taste appears at higher peroxide values than is normal in lard. A combination of BHA, ethylgallate and citric acid provided the best protection of pure lard in accelerated tests and in storage trials at 25°C. (See fig. 1).

Schönberg's neutralred test is a quick examination of stability in unrefined lard. The fatty acids of low molecular weight which are formed by the secondary processes during the oxidation will displace pH in an aqueous phase. The lard is kept in Petri dishes at 105°C, and the cooled fat is coloured by a newly made solution of the neutralred. A red colour in both daylight and ultraviolet light indicates rancid fat, while fresh fat gives a yellow colour. If this colour change occurs within one hour, the stability of the lard is less than four months at 5°C. The examination is a rough test by which one can separate less stable lard.

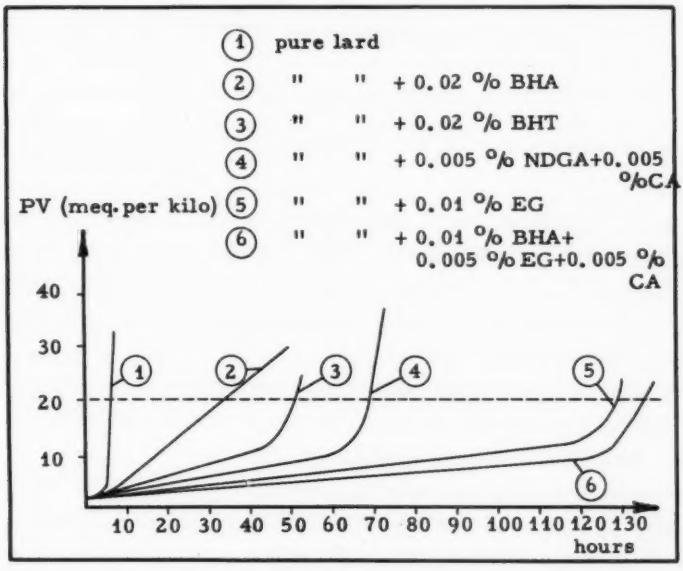

Figure 1.

AOM-stability (97.8°C).

During the course of the discussion it was stated that the lard mentioned was processed in an autoclave and a Laval centriflow system and that Danish pure lard has an iodine value of about 50.

INFLUENCE OF THE CATTLE AND ITS FODDER ON THE TENDENCY TOWARDS OXIDATION IN MILK FATS.

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Oxidative alterations in dairy products can for instance appear as a "tallowy" taste in milk and an "oily" taste in butter. Throughout the handling of milk, from the instant that it is milked to the finished milk or butter ready for consumption, it is possible, to a certain degree, to influence the oxidation rate.

It has been shown, that already at the instant that it is milked, milk has some tendency to oxidation. This does not apply to milk only, but also to the products which are prepared from it.

This seems, for instance, to appear from the fact that the oxidation defects in dairy products show considerable seasonal variations, even when the handling after milking is the same. The seasonal variation is particularly pronounced in milk for human consumption, in which the flavour defect "tallowy" appears only in the wintertime, especially in the months March-April, i.e. in the last part of the period with winter feed.

Concerning butter, the seasonal variation is less pronounced, but there is still a maximum in the summertime from May to July.

The fact that these two defects appear most frequently under very different feeding conditions has caused many hypotheses about the nature of the oxidation, but in this connection it must still be remembered, that the two products- milk and butter- have very different colloid structures which may cause different oxidation processes.

Various observations have shown, that the properties of the serum phase and those of the fat phase are important factors as regards the appearance of oxidation defects as well as the rate at which these defects will occur.

It is supposed that the content of pro-and antioxidative substances of the water phase is of major importance for the "tallowy" flavour in milk. In the case of butter, many investigations indicate that the chemical composition of the butterfat is most important.

Certain heavy metals, especially copper, are pronounced catalysts for the oxidation processes in dairy products. Seasonal variations in the copper content of butter indicate that the feeding of the cattle or the lactation period have an influence on the copper content of the milk.

Vitamin C or ascorbic acid is an important factor in the redox systems causing oxidation flavour. The vitamin C content of milk is believed to be influenced by the feeding.

It is generally supposed that unsaturated fatty acids containing two or more double bonds are especially sensitive to oxidation. The milk fat contains several acids of this type and the amount is influenced by the feeding and perhaps by the breed of cattle.

In spite of this, it is not certain that the oxidation rate corresponds to the content of easily oxidizable fatty acids in the butterfat. The reason is that butterfat may have a varying content of pro- as well as antioxidative substances. Our knowledge of the composition and effect of these substances is rather incomplete, but it is supposed that the amount is influenced by the feeding , the breed of cattle and the lactation period. This is true of the tocopherols and carotins in the fat. Often antioxidative properties are attributed to these substances, but prooxidative properties have also been observed.

Antioxidative substances have been added to the feed, and in some cases an antioxidative effect has been observed in the dairy products. In other cases no effect was found, and in a few cases a prooxidative effect occurred.

The stability of dairy products in regard to oxidation is a matter of very great economic importance. The dairies would like the above problems solved so that the tendency towards oxidation in their products could be minimized.

METHODS FOR THE DETERMINATION OF PEROXIDE VALUES.

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The problem of adopting official methods for the determination of peroxide values is put to discussion. The most simple and well-studied methods are the colorimetric thiocyanate and the iodometric methods.

In the thiocyanate method by-reactions with the participation of solvent molecules and of atmospheric oxygen may take place whereby erroneous results are obtained. Furthermore, the intensity of the ferric thiocyanate colour is dependent on the composition of the solvent, the hydrogen and the thiocyanate concentrations, and incidentally the presence of phospholipids. The composition of the solvent mixture must therefore be carefully standardized, and oxygen excluded in the reaction. The procedure outlined in the following is recommended[1]:

Five ml of a chloroform solution of the fat is mixed with 5 ml of a solution of 8 % ammonium thiocyanate in absolute ethanol, and oxygen-free nitrogen passed through the solution for 10 minutes. One drop of a 0.44 % ferrous chloride solution in redistilled water prepared by Lofthus Hills' method is added[2]. After a few minutes the passing of nitrogen is stopped, the volume adjusted to 10 ml, and colorimetric reading carried out. Blank determinations are substracted, and the results calculated by means of a standard curve constructed by a standard ferric chloride solution. The peroxide value is given as milliequivalents per gram fat.

Atmospheric oxygen must also be excluded in the iodometric method which it is recommended be carried out as in Lea's "cold" method[3] with only small modifications.

In comparing the methods it is concluded that both are quite simple and good methods giving reasonably reliable information about the content of peroxides in the fat. The thiocyanate method requires that the composition of the reaction mixture be carefully fixed. It requires the use of a colorimeter, and some standardization work, but, on the other hand, it is considerably more simple and faster than the iodometric method.

Most important is, however, that the limit of the iodometric method is not lower than about 0.1 microequivalent whereas the thiocyanate method is at least 10 times as sensitive. The most important problem is that of reliable methods for determining the very low peroxide values found in incipient rancidity rather than that of determining higher values with extreme exactitude. Since only the thiocyanate method will satisfy the first requirement, it is recommended that this method be adopted.

References.

1. GLAVIND, J. & HARTMANN, S., Acta Chem. Scand., 9, 497 (1955).
2. LOFTHUS HILLS, G. & THIEL, C.C., J. Dairy Res., 14, 340 (1946).
3. LEA, H.C., J. Soc. Chem. Ind., 65, 286 (1946).

DETERMINATION OF PEROXIDE IN RYE AND RYE CRISP BREAD.

(Application of the colorimetric ferric thiocyanate method).

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Rye crisp bread, a baked cereal product, based on whole ryemeal, yeast and salt (som types of crisp bread also with skim milk) shows, when made from undamaged grain, a satisfactory shelf-life when stored under normal conditions.

The resistibility to oxidation may be seen in connection with the anatomical structure of the rye kernel, the presence of native antioxidants and further that the lipid becomes partly bound to protein during the baking process.

Owing to its high content of unsaturated acids (oleic - linolenic - and linoleic) rye germ oil is very liable to become rancid, - and in spite of the modest lipid present in a cereal product like rye crisp bread, sooner or later some oxidation will occur which will result in a drawback as regards taste. The change in taste may, to some extent, also be due to other factors - in a sprouted and damaged rye the protein, representing four to five times the amount of the lipid, should also be taken into consideration.

The iodometric procedures for determining fat-peroxide in cereal products like rye crisp bread are not very suitable when small amounts of peroxide are present. In order to point out the existence of peroxide and to follow the oxidation under various conditions the well-known colorimetric ferric thiocyanate method has been applied (1).

The intensity of the developed colour was measured in a colorimeter, Beckman Model C, using a green filter 524 millimicrons.

The calibration curve, plotted from readings with ferric chloride (small amounts of aqueous ferric chloride solutions in benzene/methanol), ranged up to 15 micrograms iron per 10.0 ml final test solution, and the peroxide value (PV) was calculated by difference in extinction between final test solution and a blank. Peroxide value is expressed in millieq. oxygen per kilo fat.

The dependence of colour intensity on the concentration of hydrochloric acid was confirmed (Table 1), - as well as the independence of colour intensity of the iron content of the ferrous chloride solution (Table 2). The effect of changes in the given direction of the ammonium thiocyanate solution is stated in Table 3.

10.0 ml final test solution x)		
HCl	µg Fe^{3+}	pH
0.00016	3.6	
0.00023	5.4	
0.00060	9.3	
0.00365	9.9	3.05
0.01800	9.5	2.35
0.03600	9.5	1.95
0.07300	9.5	
0.10900	6.6	
0.20600	1.2	

x) theoret. amount of iron : 10.1 µg

Table 1.

Fe^{2+} - solution % Fe	µg Fe/10.0 ml final test solution	µg ferric-ion	
		Arachid-oil	H_2O_2 x)
0.024	12.0	9.4	5.3
0.051	25.5	12.7	6.7
0.100	50.0	12.9	7.2
0.447	223.5	13.1	8.7
0.921	460.5	13.1	8.8

x) theoret. equivalent to 10.0 µg Fe

Table 2.

Ammoniumthiocyanate-solution	Ammoniumthiocyanate in 10.0 ml final test solution	µg Fe^{3+} x)
15 %	0.075 %	11.6
30 %	0.150 %	12.3
60 %	0.300 %	12.4

x) Fe-solution not identical with Fe-solution in table 2.

Table 3.

The following procedure may be applied for the determination of fat-peroxide in rye crisp bread : A suitable quantity of finely pulverized material is extracted cold with benzene/methanol (7:3) by rotation for about 1 hour; an aliquot part of the clear fat-benzene/methanol solution is adjusted to 9.90 ml with benzene/methanol; one drop (0.05 ml) of the ferrous chloride solution and one drop of the ammonium thiocyanate solution are added, (both solutions prepared by Hill and Thiel's method); and after some minutes the colour is measured and compared with a blank. The fat content of the fat-benzene/methanol solution may be found in another aliquot part.

Comparisons of peroxide values from the colorimetric method and from an iodometric procedure show that the results obtained by the colorimetric method are invariably higher than those obtained by the titration procedure. Ratio colorimetry : iodometry ranged from 1.4 to 2.1 (Table 4).- Other colorimetric methods for determination of fat-peroxide give similar results (2, 3). By increasing the iron content to 0.9 % in the ferrous - chloride solution, a reaction ratio of 1.8 could be found with hydrogen peroxide against the stoichiometric ratio of 2.0 (Table 2).

Material	PV in milliequiv. oxygen/kilo fat		Ratio Col.: Iodom.
	Colorimetry	Iodometry	
Rye I	9.6	7.0	1.37
" II	8.7	5.4	1.60
" III	9.7	6.4	1.50
" IV	9.1	4.4	2.07
Crisp bread a	10.2	7.0	1.45
Graham	5.0	4.0	1.25
Crackers	3.9	2.5	1.56
Bisquit a	0.8	no reaction	
" b	1.0	" - "	
Crisp bread c (aged)	31.4	18.4	1.70

Table 4.

(a = wheat , b = oat , c = rye).

Peroxide values for an aged rye crisp bread obtained by the colorimetric method are given in Table 5 showing the reproducibility of the test.

The limit of sensitivity is assumed to be 0.1×10^{-4} milliequiv. by the described method. Testing and examination of rye and whole rye meal can be made by following the directions given above.

Rye crisp bread (aged)	2.0 ml fat-solution g fat calculated	PV
1	0.00448	58.5
2	0.00432	57.6
3	0.00433	58.9
4	0.00443	58.9
5	0.00420	58.2
6	0.00424	57.7

Table 5.

Summary.

The colorimetric ferric thiocyanate method is very suitable for the determination of fat-peroxide in cereals and cereal products - the method being rapid, simple and sensitive. The method indicates the presence of rancidity at a much earlier stage than does an iodometric procedure, and the method appears to be specially applicable to determinations of small amounts of peroxides. The method described does not give absolute correct peroxide values, - by control work where only relative peroxide values are desired the method will be very useful and practicable. In such cases the analyses can be carried out in the presence of air with sufficient accuracy.

1. LOFTHUS HILLS, G. & THIEL, C.C., J. Dairy Research, 14, 340 (1946).

2. HARTMANN, S. & GLAVIND, J., Acta Chem. Scand., 3, 954 (1949).

3. GLAVIND, J. & HARTMANN, S., Acta Chem. Scand., 9, 497 (1955).

THE EFFECT OF DAMAGED SEEDS UPON THE F.F.A. IN THE OIL.

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The formation of a moisture balance in layers of seeds having moisture content 7 % (5 mm thick) and 12.3 % (very thick compared to the former) was studied. The results are shown in fig. 1, where the rise in moisture content of the inner layer is given. Time in days.

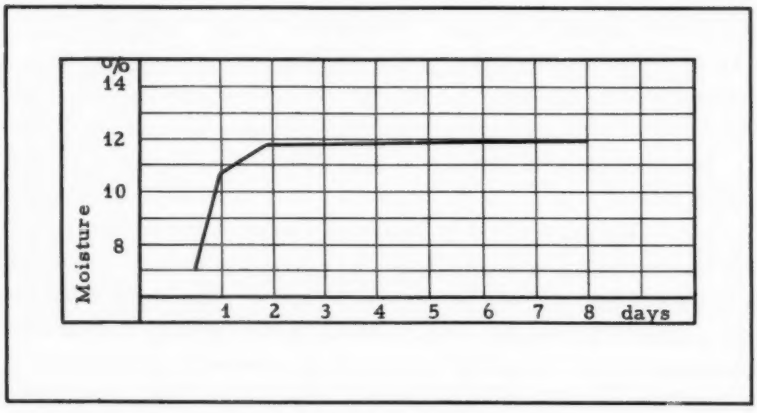
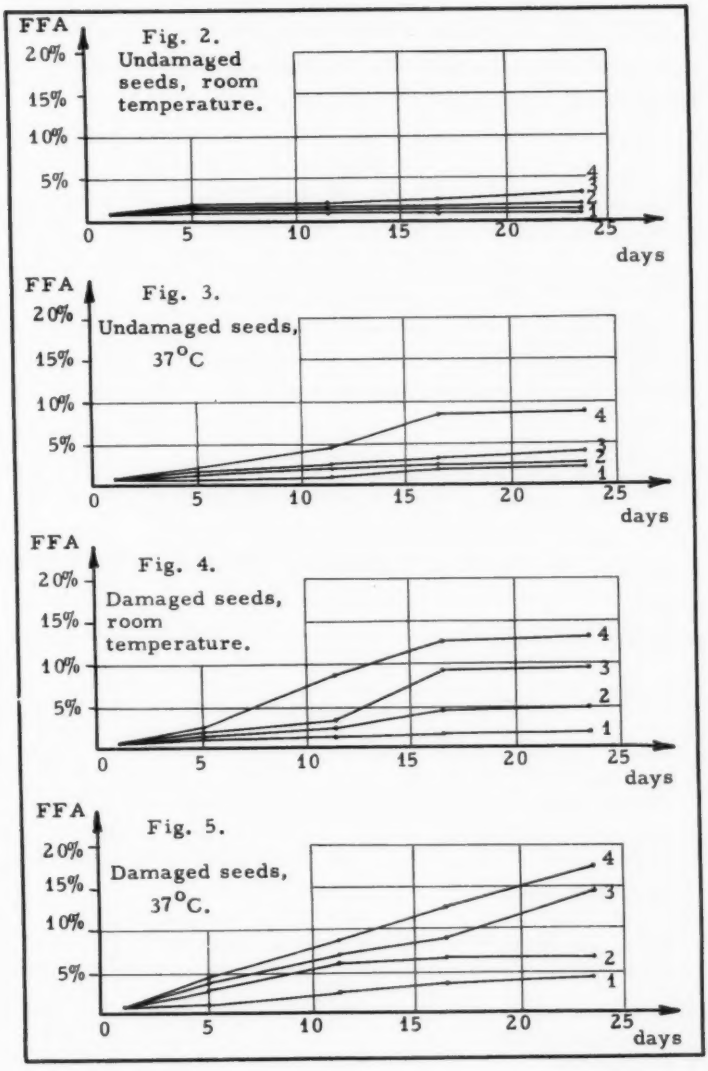


Figure 1.

Development of the moisture balance.

Artificially broken seeds, moisture cont. 7, 12, 15 and 20 % were placed in 200 g tight cans and kept at room temperature and at 37°C. Fig. 2, 3, 4, 5. The difference between enzymatic and bacteriologic hydrolysis can be seen in fig. 5, where above the critical moisture content 12 %, the hydrolysis has been strongest. Time in days.



Figures 2 - 5.

The formation of free fatty acids in damaged and undamaged seeds under various conditions.

(Moisture: 1 ~ 7%; 2 ~ 12%; 3 ~ 15% and 4 ~ 20%).

In table 1 are given results of a germination test which was carried out on moist sand in daylight at room temperature. Seeds were divided into three groups according to the length of the root. No lowering in fat content could be noticed.

Sample	Moisture %	%fat in moist seeds	FFA
Sprouted seeds with burst coats	8.0	40.5	0.72
Sprouted seeds, the root at most 2 mm	8.0	40.8	1.05
Sprouted seeds, the root at most 4 mm	8.0	41.1	1.62

Table 1.

The effect of growing on the fat content and on the content of free fatty acids in the oil.

In table 2 are given some figures taken from the seeds delivered to the plant.

	1955		
	Moisture %	% fat in moist seeds	FFA %
Sprouted seeds, the root at most 1 mm	6.9	39.2	7.9
Sprouted seeds with a long root	6.6	37.6	8.0
Sprouted seeds with burst coats	6.6	40.1	4.1
Damaged seeds	6.3	41.2	6.9
1956			
Damaged seeds from silos	7.0	39.0	3.41
1957			
Sprouted seeds, the root more than 2 mm	7.1	-	6.1
Damaged seeds	7.1	-	2.7

Table 2.

The effect of damaged and sprouted seeds on the content of free fatty acids in the oil.

FLAVOUR EVALUATION OF OILS AND FATS.

(Experience obtained from a taste panel of analytical type).

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and

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The demand which our taste and smell senses make on the deodorization process is very great. According to Evans as little as 0.1 ppm of butyr-aldehyde can be detected by taste test in mineral oil.

Certain types of taste or smell change entirely on dilution: Thus rancid soybean oils diluted with freshly deodorized soybean oil are characterized by words similar to those used for reverted soybean oils.

The problems of the analytical taste panel may be described as in fig. 1.

Fig. 2 shows the scoring scale.

type of test	result expressed by
Difference test	
D 1 without preference	identification
D 2 with "	rank
D 3 with "	points
K Quality evaluation	point-scale

Figure 1.

Problems of the analytical taste panel.

10 very good	neutral
8 good	almost neutral
6 doubtful	faint
4 poor	pronounced
2 very poor	strong

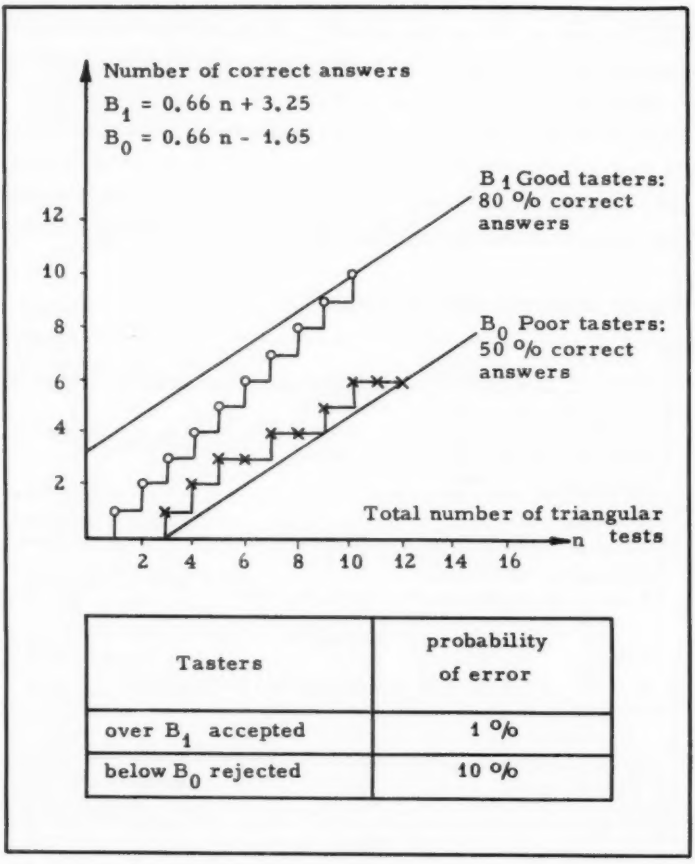
Figure 2.

The scoring scale.

For selection of a taste panel by triangular tests on oils the results are analysed according to A. Wald by sequential analysis, fig. 3.

Harries has shown that the triangular tests should be balanced with regard to the position of the single sample.

It also must be balanced as regards the type of the single sample: In triangular tests with 2 slightly rancid oils and 1 neutral oil the percentage of correct answers was significantly lower (53 %) than in similar tests with 1 rancid and 2 neutral oils (70 %).



Tasters	probability of error
over B_1 accepted	1 %
below B_0 rejected	10 %

Figure 3.
Selection of the taste panel by sequential analysis acc. to A. WALD.

By comparison of ranking versus scoring in difference tests, ranking is statistically the most correct method, but for small numbers of tastings it is somewhat less effective, fig. 4.

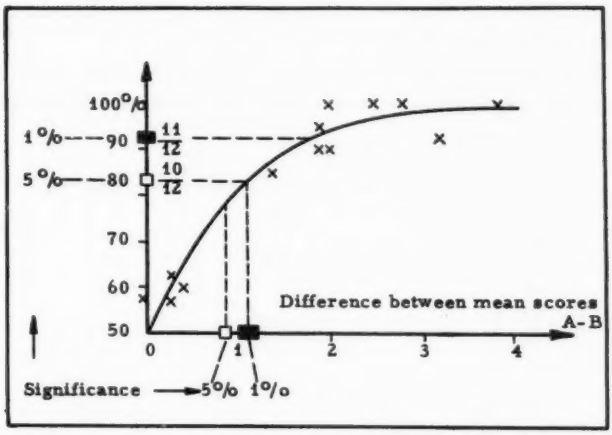


Figure 4.

Ranking versus scoring in paired comparisons of 13 different pairs of soybean oils. About 12 responses were obtained for each pair. Rank: A preferred % of total number of responses.

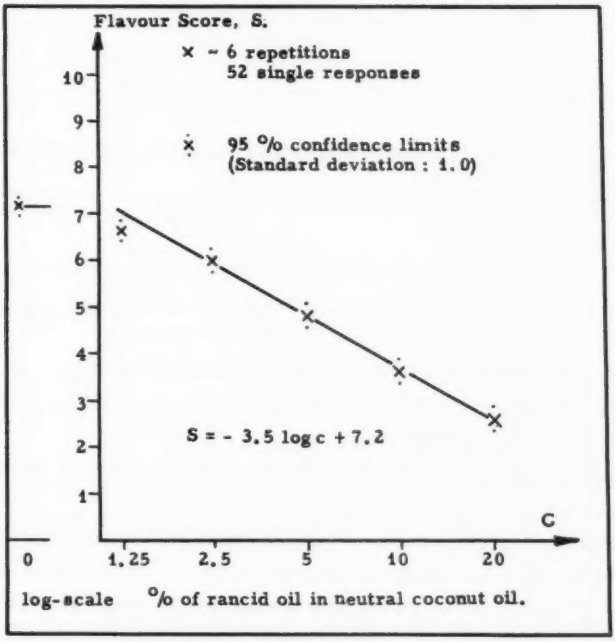


Figure 5.

Calibration curve for 6 oils to be compared at a time. (8-9 tasters).

The taste panel is considered as an instrument which indicates the intensity of off-taste (flavour) on the 10 point scoring scale. "Calibration curves", sensitivity and stability of the panel are determined, fig. 5, 6, and 7.

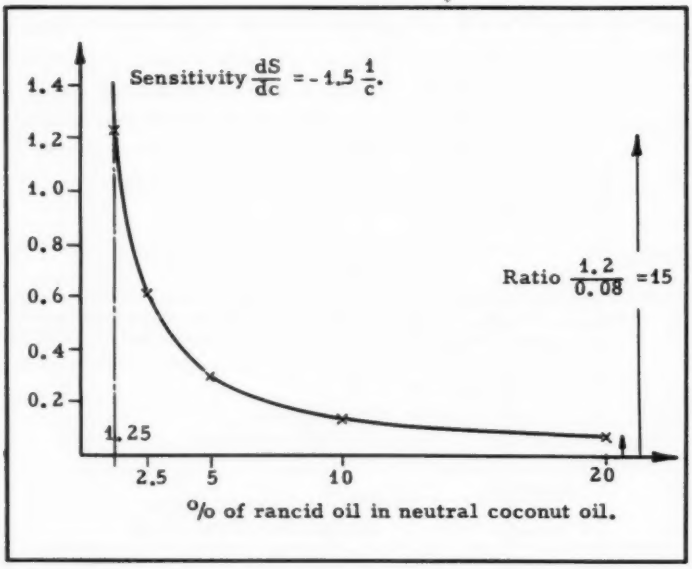


Figure 6.

The sensitivity-curve derived from fig. 5.

The tasters were well acquainted with oil-tasting, but individual differences with regard to scoring of oils on the middle and lower part of the scale still existed.

Weber-Fechner's law was found to be true for the examined oils of varying degree of rancidity.

The standard deviation of the single taste scores was - in paired comparisons of six different standard oils of varying rancidity - 1, 0 for a good oil and 1.5 for an oil of inferior quality (fig. 8). This means that the 95 % confidence limits for a single score of an oil with a "true" score of 5 are 5 ± 3, i.e. 2-8. Fig. 9 shows how the adaptation phenomena may effect the stability of the panel.

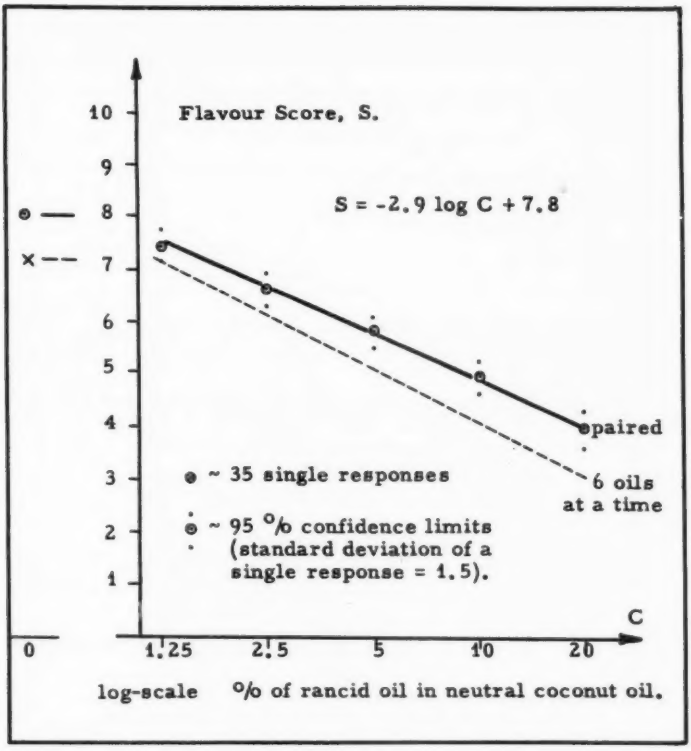

Flavour Score, S.
S = -2.9 log C + 7.8
paired
6 oils at a time
~ 35 single responses
~ 95 % confidence limits
(standard deviation of a single response = 1.5).
C
log-scale % of rancid oil in neutral coconut oil.

Figure 7.

"Calibration curve" for paired comparisons of 6 oils.

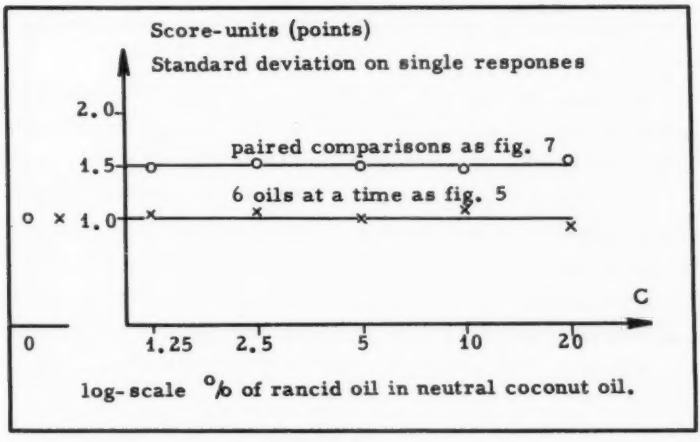

Score-units (points)
Standard deviation on single responses
paired comparisons as fig. 7
6 oils at a time as fig. 5
C
log-scale % of rancid oil in neutral coconut oil.

Figure 8.

"Stability" of the panel as found by the tests shown in fig. 5 and 7.

In order to perform statistically correct quality control regarding the taste of oils it is advisable to refer to standards of scores about 4 or 6. These standards may be made by dilution of very poor oil with neutral oil.

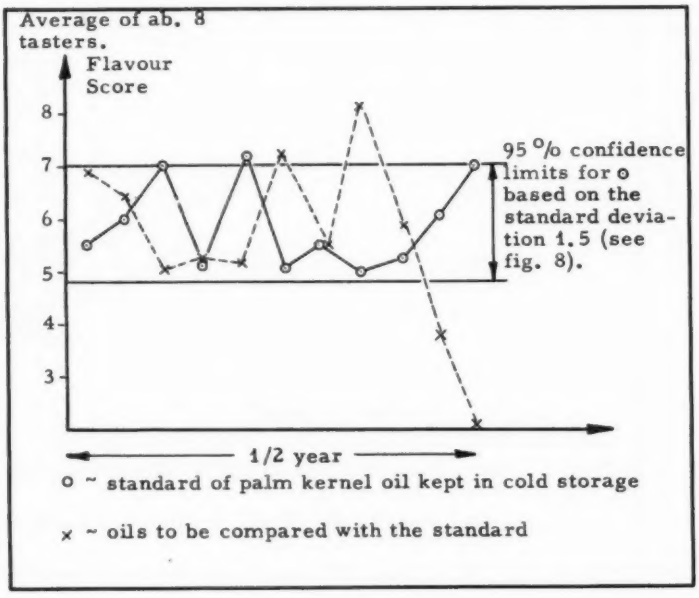

Average of ab. 8 tasters.
Flavour Score
8
7
6
5
4
3
95 % confidence limits for o based on the standard deviation 1.5 (see fig. 8).
1/2 year
o ~ standard of palm kernel oil kept in cold storage
x ~ oils to be compared with the standard

Figure 9.

Stability of the panel average for a single oil o in paired comparisons under conditions of typical adaptation.

To check the poor oil, which is stored at a low temperature, the determination of the treshold value by dilution with a neutral oil should be the best method according to literature (fig. 10).

It seems, however, as if the poor oil is characterized more exactly by determination of the dilution at which the curve of scores (points) versus dilution intersects the center line, 5 of the scale (fig. 11), than by the threshold value of 75% correct identifications by paired comparisons (the number of tastings were the same for both methods). Further investigations are needed to check this hypothesis.

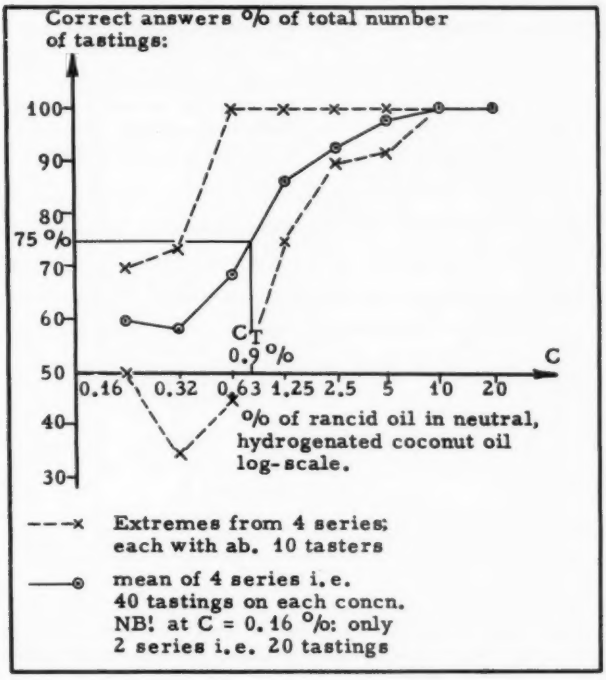


Figure 10.

Determination of the threshold value of a rancid oil by paired comparisons of a neutral, hydrogenated coconut oil versus the same oil with an addition of rancid oil.
On probability paper this curve is converted to a straight line.

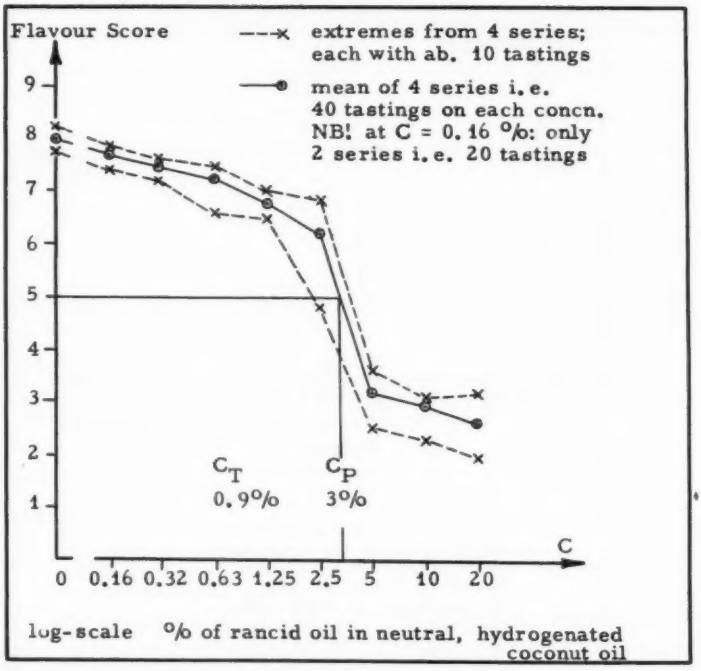


Figure 11.

Scores obtained by the paired comparisons described in fig. 10.

During the discussion it was pointed out that the oils were tasted in the melted state.

ANALYTICAL CONTROL OF OXIDATION DURING PRODUCTION AND REFINING OF OILS AND FATS.

G. WODE

Fil.dr., AB Margarinbolaget, Bromma, Sweden.

A spectrophotometrical method for estimation of carbonyl compounds has been worked out. The obtained carbonyl value is, together with the peroxide value, a good tool in controlling oxidation during the processes of oil manufacture. A paper concerning this subject has been published in the J. Am. Oil Chem. Soc., 34, 606 (1957).

BEHAVIOUR OF SOME OXIDATIVE COMPOUNDS DURING THE PROCESSING OF EDIBLE OILS.

P. MØLLER

Head of research, AB Karlshamns Oljefabriker, Sweden.

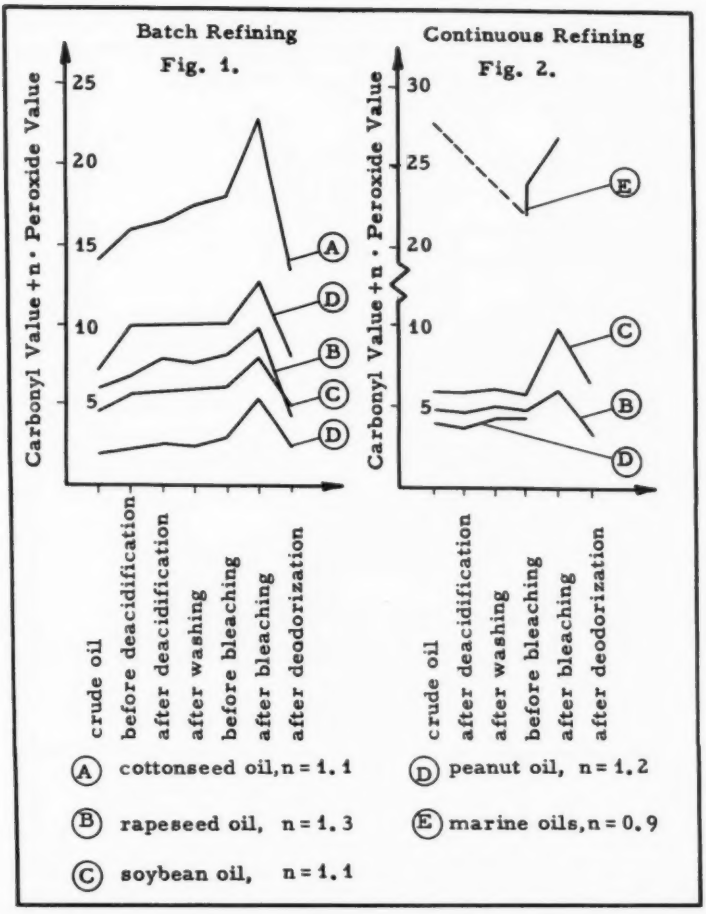
During the last two years we have applied the determination of peroxide-and α-, β-diunsaturated carbonyl-numbers (A-value according to Holm and Wode) all over our production. Peroxide values are given as mmoles/kilo and carbonyl content as equivalent to mg-% cinnamic aldehyde. The sum $A + n \cdot P$, where n is a factor for conversion of peroxides to carbonyl compounds, is to a certain degree a measure of the total amount of oxidative compounds.

It is used to control the quality of crude oils as follows: Well processed vegetable oils have A-values < 2, P tells about the storing time at low temperatures. A high A-number (A>4) indicates that either storing or processing of seeds or storing of oil has been incorrect. Excellent marine oils have A-numbers about 7 and P-numbers about 4. Essentially higher numbers indicate erroneous processing or/and storing.

As peroxides mainly are converted during bleaching it is of greatest interest to determine n during an ideal bleaching. This gives $0.8<n<1.5$. The mean value of n for different oils has been used in fig. 1 and 2, which show that in batch refining the most harmful steps are 1:heating of crude oil with air incorporated during filling of the refining kettle and 2: the bleaching step. Even the air in the bleaching earths is of importance. It is stated that oils are never so sensitive to air as in the presence of active bleaching materials, apart from the deodorization step.

As shown, continuous refining in hermetic separators is superior to batch refining in omitting the development of oxidative products.

During the hydrogenation of 600 t marine oils to 32/34°C in different ways and with oils of different origin the carbonyl content was determined every half hour and plotted against the decrease of iodine value from the start of hydrogenation. 98 % of all analyses fall within the hatched area in fig. 3. As vegetable oils show the same phenomenon it is stated that oils starting the hydrogenation with a carbonyl content between 10 and 50 very quickly decrease the same to about 8-15 units. The remaining carbonyl compounds are hydrogenated very slowly but about



Figures 1 and 2.

iodine value 100 the removal of these compounds speeds up again and leaves 1-4 units at iodine values of 70-75. Oils starting with only 10 units or less show a slow decrease too.

It is a question of greatest importance if the A-value after deodorization is a measure of the keeping quality of the oil. In the experiments on the above-mentioned marine oils $32/34^{\circ}$, the keeping quality was defined as the number of days which passed until a majority of tasters

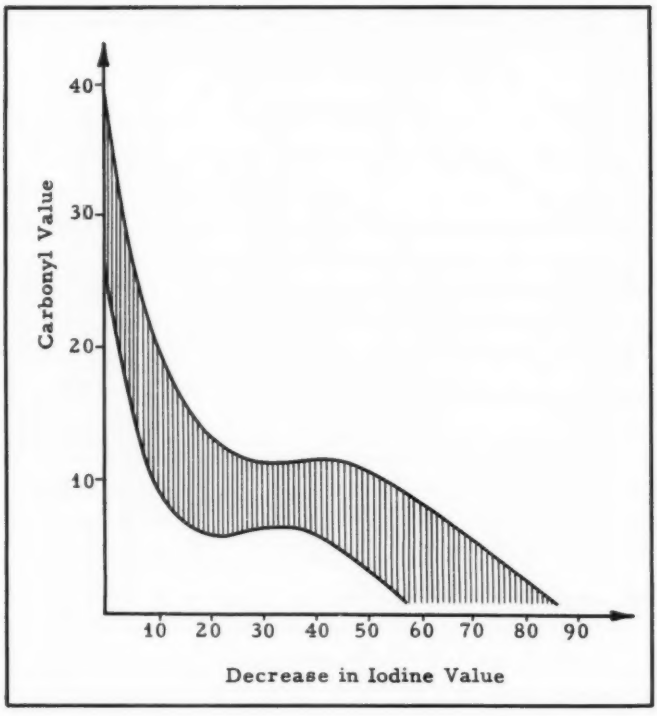
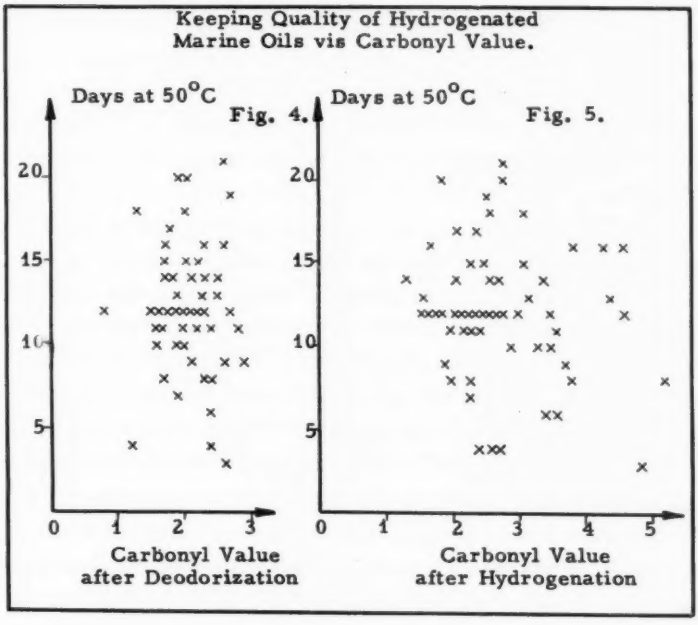


Figure 3.

judged the oil to be too bad for delivery. From fig. 4 and 5 will be seen that in the range of A-values below 3 no correlation was found between keeping quality and carbonyl content neither after deodorization nor after hydrogenation.

According to our experience, vegetable oils with a carbonyl content above 5-10 units and of hydrogenated oils above 3-5 show an unsatisfactory keeping quality. Below these limits it depends on other things as remaining quantity of antioxidants, mucilaginous materials, traces of metals etc.

Compared with the Swift test the method offers quick information and is applicable in all steps of production.



Figures 4 and 5.

HANDLING, SHIPPING AND STORAGE OF CRUDE AND REFINED EDIBLE OILS.

E. OLIN

Chief engineer, AB Karlshamns Oljefabriker, Sweden.

The shipment of crude oils is now, owing to economy, generally carried out by tankers, but the quality is better conserved in drums. During storage of fats in tanks the temperature has to be kept high enough to prevent the crystallization of solid material. It is therefore better to have a number of small tanks, having all those at low temperatures, from which oils are not withdrawn. The temperature during the melting of fat should be controlled carefully and hot water is to be prefered as the heating medium. Bad isolation causes circulation in the oil, thus increasing the rate of oxidation.

The oxidation of oils in oil seeds is much slower than in processed crude oils. Experiments with rapeseed stored in paper bags up to 8 m. high for 20 months resulted in an oil with the following data: peroxide value 1.0 millimole/kilo, aldehyde value according to Holm and Wode 0.7 mg% and total tocopherol 0.088%. A crude rapeseed oil in tanks will be oxidized already after 3-4 months at the same level. Hydrolysis is much slower in the crude oil, if it is carefully separated from all gums, moisture and residual meal. In processing copra, it is important that the portion of damaged fruits be as low as possible. The content of free fatty acids in the crushed or dusty material may be as high as 35%.

It is of importance to protect the crude oils from the very first processing steps against air and high temperature. Continuous separation of gums in hermetic centrifuges and drying in vacuo improves the quality of the crude oil. Except Japanese whale oil, marine oils normally contain a rather high amount of dissolved gums which settle in the oil during storage, thus resulting in refining difficulties in the last 10-15% of the oil. The crude oil may be according to the contract, which requests only certain values for moisture, dirt and ffa, but does not include values for gums, stearines, and oxidized materials.

It is possible to improve the keeping quality of crude rapeseed oil and groundnut oil with synergists, but not to the desired extent. A similar experiment with crude marine oils gave no improvement in the keeping quality.

The major part of refined oils is transported in tank cars at about 50°C. We used tanks cars having miscellaneous linings - tin, aluminium, plastics and even carbon steel. No difference in the quality of the oils or increase in the iron content was observed. The deliveries to the margarine manufacturers now generally involve margarine blends. This has the advantage of keeping the transportation temperature lower than with hydrogenated fats alone. Fats in minor quantities and fats for transportation over long distances are still handled in drums. Refined fats keep better in drums when they are supercooled just before tapping and solidify promptly. In connection with the re-melting certain precautions have to be observed. Experiments have been carried out on the keeping quality of salad oils in regard to the colour of the glass bottles used. The colourless bottles used earlier caused a rubberlike taste in some oils. It has been shown that the glass of the usual green-brown Swedish beerbottles, absorbing the light below 5000 Å, are satisfactory for edible oils too.

During the discussion it was mentioned that bleaching of rapeseed oil caused only a slight decrease (about 10 %) in the tocopherol content.

OXIDATION AND SELF-HEATING IN HERRING MEAL.

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Forskningsinstitut, Tjæreviken, Norway.

Herring meal is the dried residue from the production of herring oil. The presscake is not completely free from oil, so that the processed herring meal will still contain between 5 and 10 % fat. This fat is easily oxidized, and will, as soon as it is prepared, quickly absorb oxygen from the air.

The reaction may develop so vigorously that self-heating and discolouration of the meal take place. Herring meal is a highly valuable feedstuff, and in serious cases of overheating its nutritive value may be depressed (Tarr 1951).

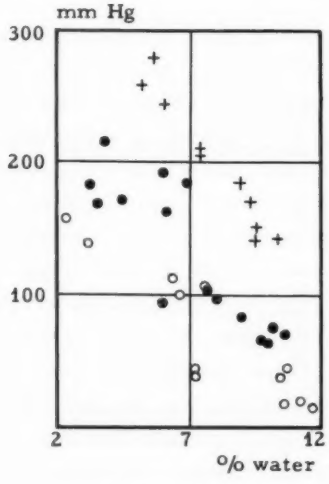


Figure 1.

Correlation between oxidation and degree of drying in herring meal processed from the same catch.

+, • flame dried meals.

o steam dried meal.

Methods taken into use for study of the conditions by which oxidation and self-heating take place are temperature measurement, oxygen absorbtion and colour development. The manometric measurement of oxygen absorbtion is found to be simple and useful, and for this reason preferred to the conventional chemical methods. Further, chemical methods for investigations on oxidation of fat in herring meal raise difficulties which are avoided by the direct method.

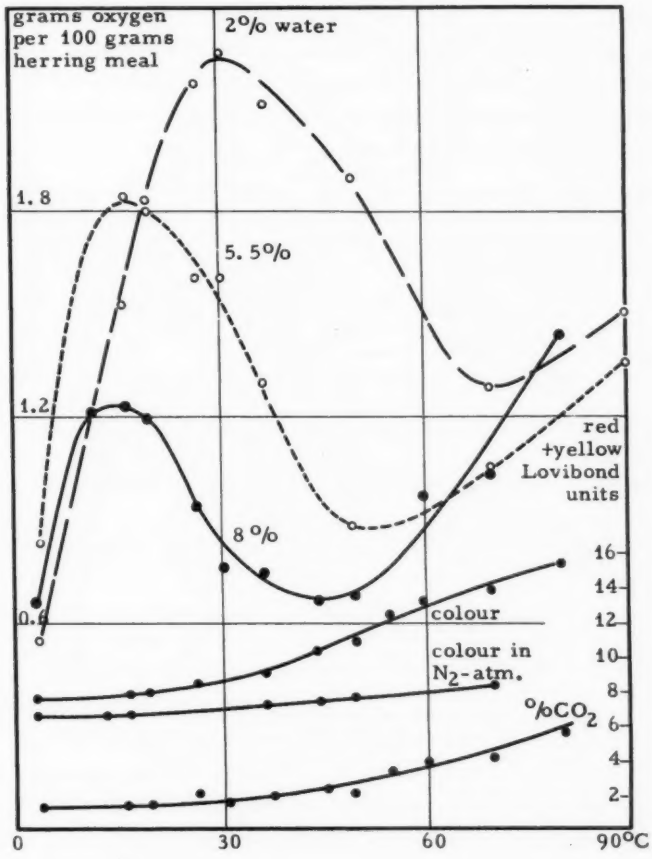


Figure 2.

The total oxidation in herring meal with 8% moisture at increasing temperatures. The dependence is compared with the behaviour of drier meals and with the formation of CO_2 and colour.

The observations show that there is a nearly straight line relationship between the degree of drying, determined by moisture content, and oxidation - determined by oxygen uptake - under otherwise constant conditions in production. Determination of the regression line is used as a method of comparing oxidation tendency in meal under varied production conditions. That the influence of drying plays a role in the succeeding oxidation does agree with earlier observations made by chemical methods on fat in herring meal. Aure (1952) finds a higher content of aldehydes in flame dried meal than in steam dried meal. The development of peroxides is more intense in sharply dried meal (Olafsson 1953).

The marked relationship is suggested due to activation in the dryer and antioxidative action of water.

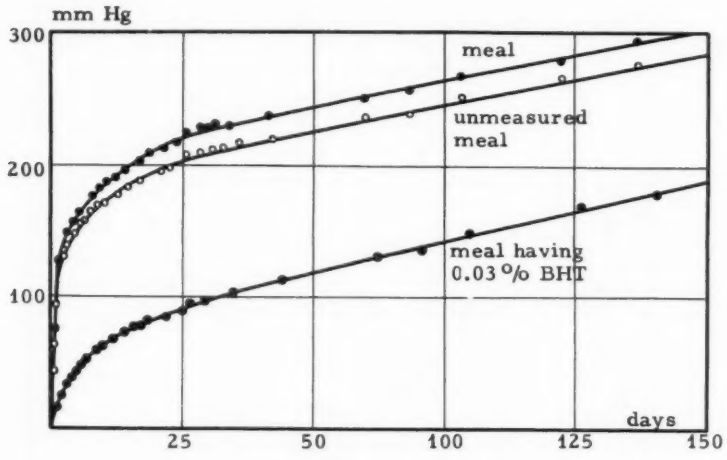


Figure 3.

The progress of oxidation in herring meal under oxygen: Effect of milling and of BHT.

Our measurements show that oxidation proceeds at a high rate the first day after production, and that the reaction is very slow after one month - under free access of oxygen. An amount of oxygen in the order varying from 5 to 20 % of fat weight is taken up during this first period.

Oxidation is, to a lesser degree, dependent on grinding. It is dependent on oxygen pressure, and reaction temperature. The progress of oxidation differs with increasing temperatures. A minimum range is observed and suggests formation of antioxidants in the meal with elevated temperatures.

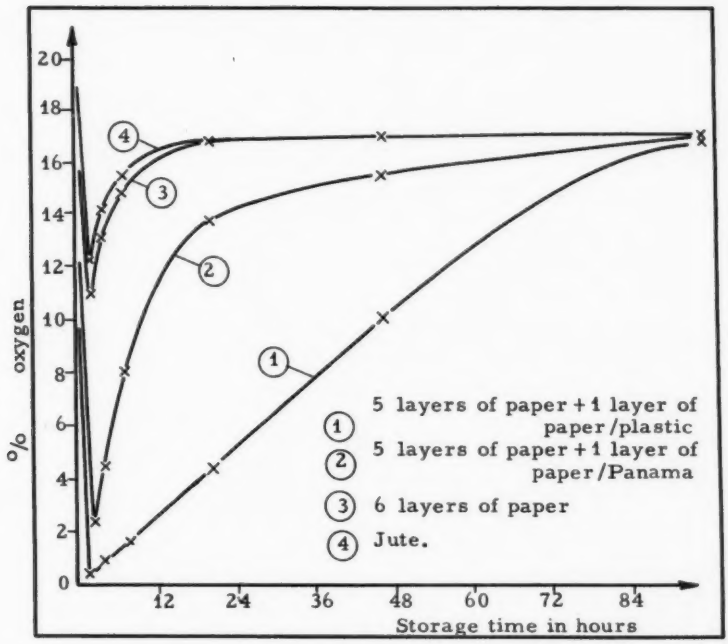
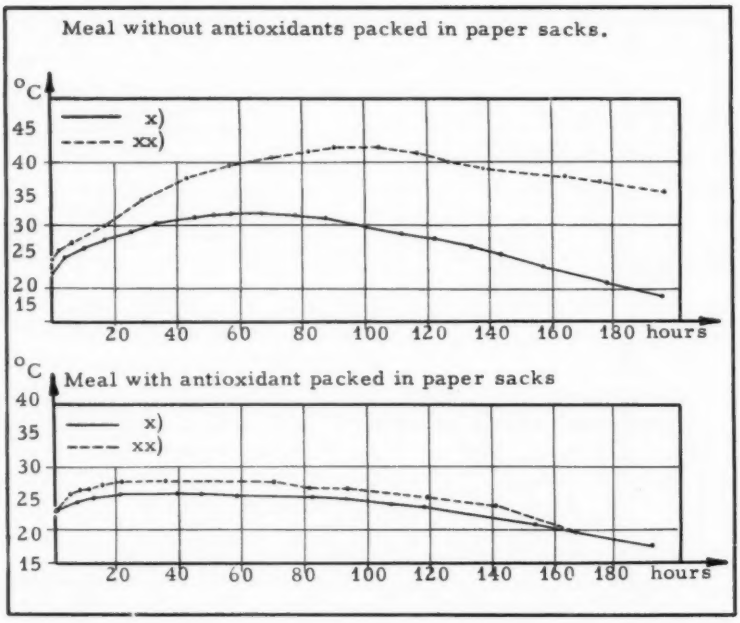


Figure 4.

Change in oxygen content of air in herring meal during the first days after production. Effect of different types of bags.

Development of browning depends on heating and the presence of oxygen. Oxidation, with related factors, are important for the resultant colour of herring meal.

Work with the problem of self-heating has, besides studies of its nature and influencing factors, aimed at finding a general means of reducing autoxidation and slow the reaction. Tests with plastic impregnated bags and with antioxidants have given promising results.



x) Average temperature in stacks.

xx) Maximum temperature in stacks.

Figure 5.

Heating of experimental lots of 30 tons herring meal.
Effect of 0.03 % BHT added after drying.

SOME FACTORS INFLUENCING THE OXIDATION STABILITY AND FLAVOUR OF DEODORIZED SOYBEAN AND RAPESEED OIL.

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Tekn.lic., AB Separator, Stockholm, Sweden,

and

M. NYMANN

Engineer, AB Separator, Stockholm, Sweden.

Modern refining of vegetable oils generally includes alkali refining in one or two stages, water washing, bleaching, and deodorizing.

It is well known that contact with air should be avoided when bleaching and deodorizing the oil. The influence of oxidation in the neutralizing and washing stages, which both take place at considerably lower temperatures, has however, usually been disregarded.

In the present investigation a number of soybean and rapeseed oils has been alkali refined, the oils being either exposed to air or protected from oxidation during neutralization and water wash. The oxidative conditions chosen were roughly the same as could be expected in commercial batch refining or in continuous refining in centrifuges of the so-called "open type", where the oil is mixed with air when entering and leaving the separator bowl.

The neutralized oils which showed characteristic variations in the peroxide values were bleached and deodorized under strictly uniform conditions and the oxidation stability was determined. This was done by blowing the oil, which was kept in darkness at 40 ^{o}C, with oxygen, and by following the increase of the peroxide value. When defining the oxidation stability as the time period that elapses before the peroxide value reaches a given level, e.g. 10 or 30 meqv./litre, a direct proportionality was found between the peroxide value of the washed and neutralized oil and the stability of the corresponding bleached or deodorized oil. This relationship is shown in fig. 1.

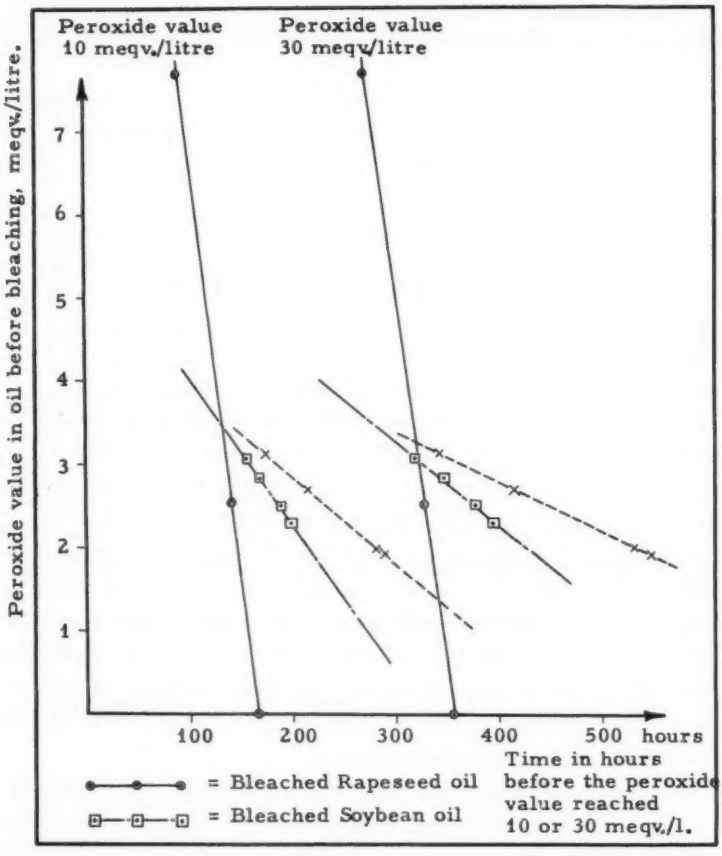

Figure 1.

Relationship between peroxide value of neutralized and washed oils and oxidation stability of the corresponding bleached and deodorized oils.

The results of the investigation indicate that contact with air should be avoided during neutralizing and washing, as even a small increase of the peroxide value during these treatments causes a deterioration of the oxidation stability of the bleached and deodorized oil. In continuous refining this deterioration can be avoided by the use of centrifuges of the so-called "hermetic type".

It is well known that small amounts of phosphatides which cannot be removed even by repeated treatments with lye often remain in neutralized and washed soybean and rapeseed oils. According to the experience of the present authors but in contrast to frequent statements in current literature, any lecithin content of the neutralized oil is detrimental to the oxidation stability and the flavour of the bleached and deodorized oil.

Kind of oil	Treatment besides neutralization and water wash	Peroxide value before bleaching, meqv./litre	Phosphatide content after bleaching o/o	Oxidation stability of bleached, deodorized oil expressed as peroxide value (meqv./l) in oxidized oil after certain time intervals				Flavour score x)
				100 h.	200 h.	300 h.	500 h.	
Rapeseed	None	4.35	0.111	22.8	40.5	-	-	1
do.	Re-refining with mixture of lye and sodium carbonate	5.20	0.011	7.1	16.5	20.3	-	3
do.	Pre-treatment with conc. phosphoric acid	4.54	0.001	2.1	3.0	2.8	2.5	5
Soybean C	None	2.05	0.108	30.0	-	-	-	1
do.	Re-refining with mixture of lye and sodium carbonate	2.46	0.001	2.3	5.7	13.4	39	5
do.	Pre-treatment with conc. phosphoric acid	1.53	0.009	1.4	4.3	10.4	32.1	5
Soybean D	None	7.81	0.002	2.0	3.5	4.8	5.4	1
do.	Re-refining with mixture of lye and sodium carbonate	10.30	0.002	1.3	2.5	2.6	2.6	3
do.	Pre-treatment with conc. phosphoric acid	9.05	0.002	1.7	2.2	1.4	1.7	5

x) 1 is a bad score and 5 a very good one.

Table 1.

Influence of residual phosphatide content in neutralized oils on oxidation stability and flavour of bleached and deodorized oils.

As may be seen from table 1, the phosphatides may be completely removed by treating the oil with 0.05 - 0.2% of concentrated phosphoric acid prior to the neutralization, or by re-refining the neutralized oil with a mixture of lye and sodium carbonate.

Both treatments removed the phosphatides completely and improved the oxidation stability and flavour of the deodorized oils considerably. In the two last mentioned respects the pre-treatment with phosphoric acid was superior to the re-refining with lye and sodium carbonate.

Another soybean oil where the phosphatides could be completely removed by simple alkali refining yielded a deodorized oil with a good oxidation stability. Even for this type of oil an improvement of stability and flavour was, however, obtained by any of the two supplemental treatments.

Pre-treatment with many other acids, such as citric acid, tartaric acid or acetic anhydride, has also been investigated but none of these agents have given the same improvement of the oxidation stability and flavour as phosphoric acid.

PRACTICAL RANCIDITY PROBLEMS IN THE PRODUCTION OF MARGARINE.

E. EVENSEN

Chief chemist, A/S Borgar margarinfabrikk,

Frederikstad, Norway.

Every oil producer and scientist tackling problems connected with stability of fat should be familiar with the different steps in margarine production.

(In Scandinavia nearly no margarine factory has its own refinery).

We have obtained very good results with direct contact with our oil and fat producers. The fat raw materials used in Norway are: Hardened whale oil, refined coconut oil, groundnut oil and soybean oil. Tests show that special care must be taken with each of them during transport, storage and margarine making.

Coconut oil is rather stable at 60 °C in darkness and nearly so stable are hardened whale oils mp. 30/32 °C and 38/40 °C.

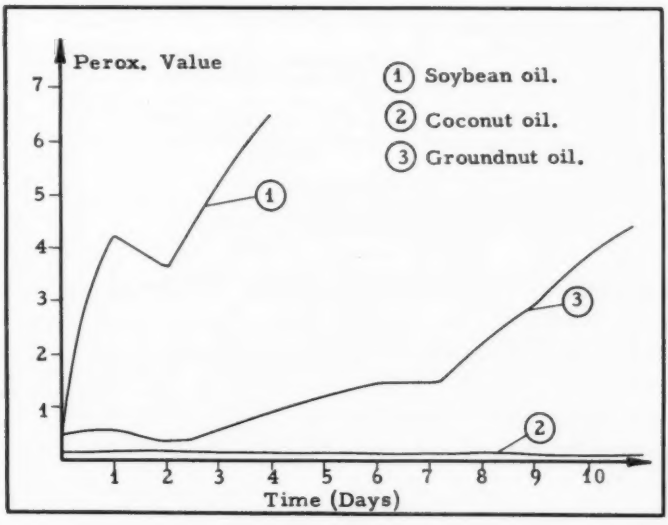

Figure 1.

Determination of peroxide value at 60°C.

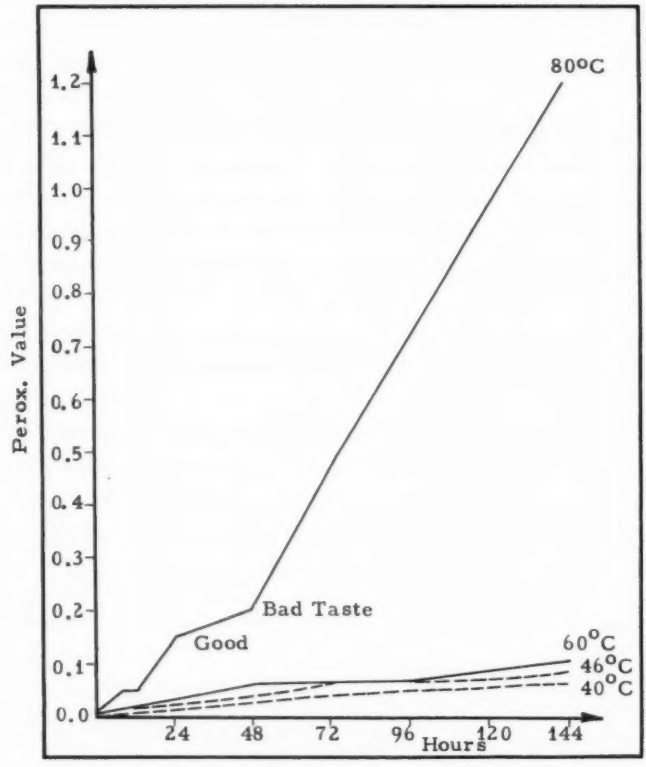

Figure 2.

Hardened Whale Oil 30/32°C.
Stored in Glass at 40°C, 45°C,
60°C and 80°C (Dark Place).

Refined groundnut oil and soybean oil will not be stable for normal storage time at a temperature so high as 60°C, as these oils should be kept at a temperature not higher than common room temperature. 60°C seems to represent an upper limit for hardened whale oil and coconut oil.

All fats must be protected against light. We have not found sufficient information about the different wavelength's activity in fat spoilage, but we have found that defused sunlight passing double window glass and a wall of a Pyrex-beaker will give a terrible off-flavour to the hardened whale oil in a few minutes (figure 3).

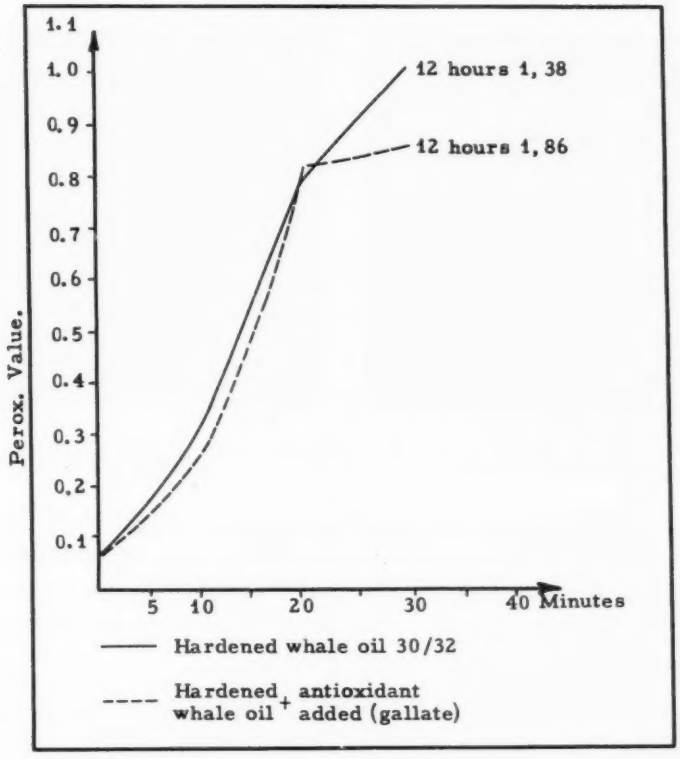

Figure 3.

Increase in peroxide value for hardened whale oil exposed to sunlight through glass.

In a modern margarine factory you will find aluminium and stainless steel all over the plant and it would be great progress if every oil factory would use resistant metals (aluminium or stainless steel) in all pipelines, tanks and pumps used for ready refined and deodorized fat.

The most important places are the filling stations where the fat can be kept for some hours.

All transport cars must have aluminium tanks.

Drums made of pure iron will give special problems. The oil producers ought to get aluminium drums or another type of drum made of resistant material.

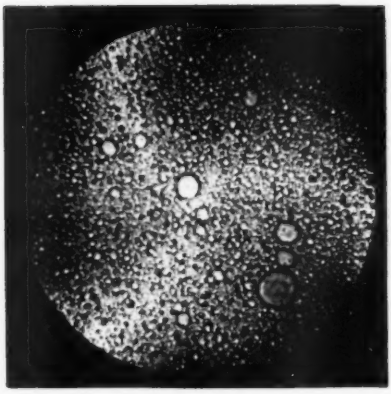

Figure 4.

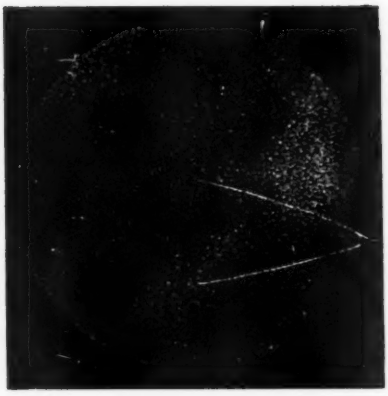

Figure 5.

In a modern margarine plant the margarine emulsion will be chilled, treated and packed in a closed system, and this will reduce the risk of infection from the air. Water droplets will have smaller diameters (Fig. 5) than we find in margarine made in the old way with cooling drum and vacuum kneader (Fig. 4).

The reduction in the diameter of the water droplets will increase the contact area between the fat and water phases and this seems to increase the fat oxidation.

Special care must be taken to choose the best quality of the other raw materials as milk, water, salt, colour, vitamins and so on, and it would be of great value if the producers of these raw materials too were familiar with the production of margarine. We like to make our margarine without antioxidants and preservatives, and brands sold in Norway for normal household use have no need of such chemicals.

		1 hour		3 hours		24 hours		48 hours		72 hours	
		Flavour	P.ox. val.	F.	P.V.	F.	P.V.	F.	P.V.	F.	P.V.
Uncovered		Good	0.05	G	0.05	Beg. rancid	0.36	Rancid	0.74	R	0.85
Greaseproof	43g/m^2	G	0.05	G	0.05	G	0.32	G	0.38	R	0.65
Pergaloid (Parchment Substitute)	62g/m^2	G	0.04	G	0.05	G	0.20	Beg. rancid	0.31	R	0.63
Transparent Parchment	60g/m^2	G	0.03	G	0.05	G	0.16	G	0.36	R	0.79
Opaque Parchment	63g/m^2	G	0.03	G	0.04	G	0.14	G	0.33	Beg. rancid	0.46
Al-Foil	67g/m^2	G	0.02	G	0.02	G	0.04	G	0.04	G	0.10

Figure 6.

Testing the margarine surface.
Lighting tube: common type 4000-7000 Å.
Distance from the margarine surface: 30 cm.

		1 hour		3 hours		24 hours		48 hours		72 hours	
		Flavour	P.ox. val.	F.	P.V.	F.	P.V.	F.	P.V.	F.	P.V.
Uncovered		Rancid	0.10	R	0.30	R	1.16	R	4.07	R	4.60
Greaseproof	43g/m^2	Good	0.05	R	0.10	R	0.11	R	0.25	R	0.77
Pergaloid (Parchment Substitute)	62g/m^2	G	0.05	G	0.07	R	0.14	R	0.22	R	0.49
Transparent Parchment	64g/m^2	G	0.03	G	0.04	G	0.12	R	0.28	R	1.25
Opaque Parchment	63g/m^2	G	0.02	G	0.02	G	0.10	G	0.10	R	0.31
Al-Foil	67g/m^2	G	0.01	G	0.02	G	0.06	G	0.03	G	0.19

Figure 7.

Testing the margarine surface.
Sterielectric lamp - 94% - 2536,5 Å.
Distance from the margarine surface: 30 cm.

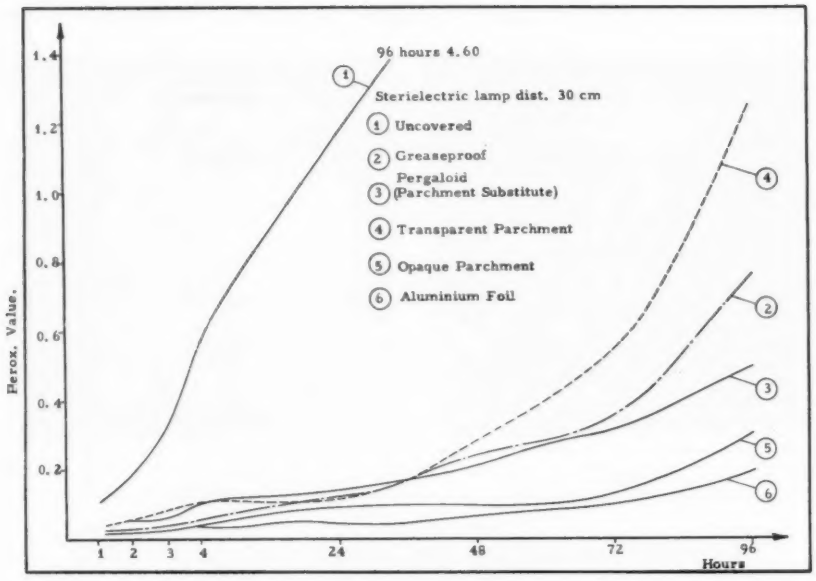

Figure 8.

Diagram based on figure 7.

We think there is plenty of work to do with the hygienic standard and the use of resistant equipment in oil factory and margarine plant that will give a higher stability to margarine, before we find it necessary to discuss the use of antioxidants in margarine production.

We also tested the degree of protection given by wrappers and found aluminium foil to be the best, but vegetable parchment filled with titandioxide will give sufficient protection for normal brands. Perhaps it would be useful to impregnate the wrappers with antioxidants and preservatives.

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